

Chapter 8

Methods for Measuring Atmospheric Nitrogen Deposition Inputs in Arid and Montane Ecosystems of Western North America

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Abstract

Measuring atmospheric deposition in arid and snow-dominated regions presents unique challenges. Throughfall, the flux of nutrients transported in solution to the forest floor, is generally the most practical method of estimating below-canopy deposition, particularly when monitoring multiple forest sites or over multiple years. However, more studies are needed to relate throughfall fluxes to total atmospheric deposition, particularly in seasonally dry regions. In seasonally snow-covered regions, the distribution of atmospheric deposition and subsequent nitrogen (N) fluxes are highly sensitive to the temporal and spatial dynamics of snow accumulation and melt. Recent developments in passive monitoring techniques for throughfall and measurement of gaseous pollutants greatly facilitate monitoring of atmospheric deposition and ambient pollutant concentrations over broader spatial scales than was previously possible. Here we focus primarily on N fluxes as N is both a limiting nutrient and a pollutant in many terrestrial ecosystems, and because sulfur (S) deposition is not a widespread problem in the West. Methods suggested for estimating spatially distributed atmospheric deposition in arid and snow-dominated systems include simulation modeling, inferential method, throughfall collection, branch rinsing, N accumulation in surface soils of arid zones, and snowpack sampling methods. Applying more than one approach is often necessary to capture the various atmospheric deposition pathways and the spatial and temporal variability of N deposition.

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8.1. Introduction

In recent years, our understanding of nitrogen (N) deposition effects in ecosystems of western North America has increased considerably, although in some areas of the West, near large emission sources, deposition rates and ecological effects are poorly understood. In order to understand the effects of atmospheric deposition on ecosystems or to determine the effectiveness of emissions control strategies, suitable methods of measuring deposition inputs are needed. In many instances, N loading to ecosystems of western North America is either unknown or highly uncertain. This is largely because of the technical and logistical difficulties of measuring atmospheric deposition in systems that are either dominated by dry deposition or in the case of high-elevation systems, where measuring deposition is difficult because of remoteness, lack of electric power, severe weather conditions, widely fluctuating snow levels, and dilute pollutant concentrations in large volumes of precipitation (Weathers *et al.*, 2000, 2006).

Various approaches are needed to measure N deposition in arid and montane ecosystems of western North America (Table 8.1). Selection of appropriate techniques is based on the predominant climate and ecosystem conditions, the number of sites to be monitored, the accuracy needed in the measurement, the geographic scale of the area to be monitored, cost considerations, and the level of technical expertise available. Existing national deposition networks (see Section 8.2.6) are useful in tracking long-term trends in atmospheric deposition; however, data from these networks are often of limited usefulness in studies of N deposition effects in western ecosystems.

The purpose of this chapter is to provide an overview of methodologies for measuring atmospheric deposition under conditions prevalent in western North America, with particular emphasis on high-elevation ecosystems that are seasonally snow covered, and on arid and semiarid ecosystems with a major dry deposition component. Information on chemical, spatial, and temporal aspects of N deposition in snow or dry deposition onto snow is another aspect that is important in evaluating ecological effects and will also be treated in this chapter. The major focus of the chapter will be on N deposition, but deposition of sulfur (S) is also briefly considered. Dry deposition methods have been reviewed previously (Lovett, 1994; Lovett & Lindberg, 1993; Wesely & Hicks, 2000); thus, our focus will be on particular challenges and methods to apply in western systems, on the use of passive samplers for gaseous pollutants and for measuring deposition in throughfall and precipitation, and on

Table 8.1. Comparative advantages and disadvantages of the atmospheric deposition methods discussed in this chapter

Method	Application	Advantages	Disadvantages	References
Wet deposition	To measure deposition in precipitation, excluding dry deposition	Is the method most amenable to comparative measurements at multiple sites, including networks	When only wet deposition is measured such as in the NADP network, total deposition is grossly underestimated in arid systems. Samplers usually require electric power. Under collection of precipitation is common, especially under windy or snowy conditions	Dämmgen et al. (2005), NADP site: http://nadp.sws.uiuc.edu/ , Erismann et al. (1994), Glaubig and Gomez (1994) (flip-top collectors that do not require electric power), Krupa (2002), Williams et al. (1998)
Bulk deposition	Also used to measure deposition in precipitation, but the collector opening is continuously exposed to the atmosphere	Electric power not required; inexpensive collectors that can easily be replicated	Mostly collects wet deposition, but varying amounts of dry deposition to the sampler are also collected. Under collection of precipitation is common, especially under windy or snowy conditions. Contamination from bird droppings can be a problem	Dämmgen et al. (2005), Erismann et al. (1994), Erismann and Draaijers (1995), Mosello et al. (1988)
Throughfall	Usually collected as bulk throughfall, in which the collectors are continuously open	Provides data on nutrient solution fluxes to soil. Deposition fluxes are based on surface area properties of native vegetation. Deposition fluxes include inputs from precipitation, dry deposition, and cloudwater. Total atmospheric deposition can be calculated from throughfall flux data, but the canopy budget models in use are still highly uncertain	Unknown amounts of deposited compounds are retained by the canopy, thus fluxes are underestimates of total atmospheric deposition. Underestimates may be greater in arid zones where long precipitation-free periods occur. Atmospheric deposition to the forest floor and understory vegetation usually not measured. Difficult to collect throughfall in arid zones with low-lying vegetation due to dust contamination	Bleeker et al. (2003), Draaijers and Erismann (1995), Erismann and Draaijers (1995), Fenn et al. (2000), Lovett and Lindberg (1993), Thimonier (1998), Weathers et al. (1995, 2006)

Table 8.1. (Continued)

Method	Application	Advantages	Disadvantages	References
Branch washing	To measure dry deposition fluxes to foliar and branch surfaces	During precipitation-free periods, deposition fluxes to native vegetation can be estimated; this is particularly advantageous in arid zones	Requires considerable amount of ancillary data to calculate annual deposition fluxes to a forest stand. Not applicable if fog or a rain event occurs during the monitoring period. As with throughfall, unknown amounts of atmospherically deposited compounds are retained by vegetation, leading to underestimates of total deposition. In arid zones, during extended dry periods, branch rinsing may overestimate dry deposition fluxes	Fenn and Bytnerowicz (1997), Marques et al. (2001), Shanley (1989)
Inferential	Used to calculate dry deposition fluxes	With adequate data collection is considered the best method of estimating dry deposition to natural ecosystems	Requires intensive data collection (meteorology, LAI by species, and frequent monitoring of all major pollutants). As a result, it is costly to implement at multiple sites, although the use of passive samplers can extend the number of sites monitored (Schmitt et al., 2005). Deposition velocity values used in calculations are often uncertain	Erismann et al. (1994), Lovett (1994), Lovett and Lindberg (1993), Wesely and Hicks (2000)
Soil accumulation	Used to measure accumulation of dry-deposited pollutants in bare soils of arid systems	Provides data on accumulation of pollutants in surface soils during dry periods. An important deposition pathway for ecosystems with bare soils	Mainly useful only during the dry season as precipitation leaches ions to deeper soil layer	Padgett et al. (1999)

Passive soil sampler	A thin soil layer in a plate for measuring dry fluxes to native soil; also soil samplers with thin soil layer glued to a disk (see Section 8.2.7)	Can estimate deposition fluxes to native soil, even over short time periods (days)	Only useful for dry deposition flux measurements	Padgett and Bytnerowicz (2001), M.E. Fenn (unpublished data)
Passive samplers	Used to obtain a time-averaged atmospheric concentration	Simple to use, inexpensive, does not require electric power; allows for replication at multiple and remote sites, thus providing information on spatial trends in atmospheric exposures	Gives only average concentrations, which obscures diurnal and other temporal trends	Bytnerowicz et al. (2001, 2005), Krupa and Legge (2000), Tang (2001)
Ion exchange resin (IER) column samplers	Used to collect ions from bulk deposition and throughfall; ions are collected by IER columns	Obviates the need for event-based or frequent collection of liquid samples, making it possible to expand the number of collectors installed in the field with reduced logistical and analytical costs	Cannot measure pH of throughfall or bulk deposition samples. Not designed to measure ionic concentrations of samples	Fenn and Poth (2004), Simkin et al. (2004)
Simulation modeling	Simulated deposition based on atmospheric emissions, atmospheric transport and chemical transformations, and deposition processes	Provides complete spatial coverage over the modeled domain; can simulate deposition through multiple pathways; can forecast future conditions including the effects of emissions reductions	Validity of results must be verified with field sampling; Models are incomplete and can have compensating errors. Elaborate statistical methods needed to compare model grid output to point-based observations	Pleim et al. (2001), Swall and Davis (2006), Tonnesen et al. (2003)

Table 8.1. (Continued)

Method	Application	Advantages	Disadvantages	References
Empirical deposition modeling	To estimate deposition over heterogeneous landscapes ranging in size from 100s to 1000s of kilometers	Based on field data; uses existing monitoring data to anchor the landscape deposition maps; results are spatially explicit, identifying hot and cold spots	Over larger scales (e.g., 500 km up to continental scale) uncertainties become large	Holland et al. (2005), Weathers et al. (2006)
Snowpack sampling	Snowpack is sampled prior to snowmelt to estimate wintertime wet deposition and dry deposition to the snowpack in sites where snow accretion occurs in winter	Best method for estimating atmospheric deposition in winter in high-elevation remote sites	Deposition estimates may be in error due to sublimation losses or snowmelt leachate losses in some sites. Logistically difficult. Dilute concentration of samples requires special care in sample collection and analysis	Clow et al. (2002), Turk et al. (2001)
Lichen bio-monitoring	Concentrations of N and S in lichen tissue provide a surrogate measure of deposition	Provides biologically relevant data, particularly when combined with data on changes in lichen communities	Does not provide direct wet or dry deposition estimates; Nutrient accumulation is species specific	Fenn et al. (2003a, 2007, 2008), Geiser and Reynolds (2002)

simulation and empirical modeling approaches for estimating deposition fluxes over broad landscapes.

8.2. Measuring atmospheric N deposition in arid systems

In arid systems, prolonged periods without measurable precipitation constitute the major factor influencing deposition processes and approaches to quantifying deposition. Dry deposition processes predominate under these conditions. Dry deposition occurs to all surfaces in an ecosystem, and deposition varies based on vegetation type and the amount of surface area. The major difficulty in measuring dry deposition of atmospheric pollutants is that deposition fluxes are influenced by factors such as the dynamic mix of pollutant species (each with its own range of deposition velocities and concentrations), physical and chemical characteristics of surfaces, and meteorological conditions (Weathers et al., 2006). Because of the large amount of data needed to calculate these deposition fluxes, throughfall is commonly used as an integrative technique to evaluate pollutant deposition (Bleeker et al., 2003). Throughfall is the water that washes from canopies to the forest floor. Its chemistry is a combination of wet, dry, and fog inputs through atmospheric deposition and what has been leached from the canopy. When there is little or no precipitation for successive months, no throughfall is collected. Therefore, throughfall measurements likely underestimate total deposition in arid systems to a greater degree than in mesic systems (Fenn et al., 2000). Thus, multiple approaches used in conjunction are sometimes needed to quantify total annual N deposition in western ecosystems.

8.2.1. Inferential method

The inferential method will not be covered in detail because it is well described in the literature (Erisman et al., 1994; Lovett, 1994; Lovett & Lindberg, 1993; Wesely & Hicks, 2000). In brief, the inferential method consists of calculations of dry-deposition fluxes to the ecosystem based on measurements of atmospheric concentrations of the pollutants of interest, the deposition velocities of these pollutants, meteorological conditions, the surface area, and the physical characteristics of surfaces. The inferential method is highly appropriate for arid and semiarid systems because of the importance of dry deposition in these systems. The inferential method has also been used effectively to better understand canopy interactions of dry-deposited species, and in

particular, to determine the extent to which throughfall measurements of deposition differ from total deposition in polluted environments because of canopy-pollutant interactions (Erisman & Draaijers, 1995; Lovett & Lindberg, 1993). Total deposition to the ecosystem can be determined by including precipitation inputs as wet deposition measurements. In areas where deposition in fog or cloud water occurs, this must also be measured if total deposition is to be determined. Deposition in fog can be important even in semiarid regions influenced by marine fogs or at high elevations where clouds come into contact with vegetation (Weathers, 1999).

Data requirements are intensive when using the inferential method to quantify N deposition. Many pollutants must be measured continuously or semicontinuously throughout the year if annual inorganic N deposition inputs are to be calculated. Continuous measurements of nitric acid (HNO_3) vapor and ammonia (NH_3) concentrations are very difficult to make, and deposition velocities for the various pollutant-plant species combinations are often unknown, requiring the use of estimated values from the literature. Also, considerable ancillary data are needed concerning meteorological conditions and surface area properties such as leaf area index (LAI) by species (Baumgardner et al., 2002). Lastly, organic N loading is not quantified, but can be an important component of annual N loading in many montane systems of the West (Sickman et al., 2001).

8.2.2. Throughfall and branch washing

Throughfall deposition is a commonly applied method of estimating pollutant deposition to forest ecosystems (Bleeker et al., 2003) and allows for the quantification of all forms of N deposition to the forest floor. Many studies have shown that throughfall deposition of S is a reasonable estimate of total S deposition (Erisman & Draaijers, 1995; Johnson & Lindberg, 1992; Weathers et al., 2006). However, in many areas, N deposition in throughfall is a lower-bound estimate of total N deposition because of canopy uptake of atmospheric N. In mesic forests, throughfall has often been shown to underestimate total N deposition by 25–40% (Fenn & Bytnerowicz, 1997; Lovett & Lindberg, 1993). In arid zones with prolonged dry periods, foliar surfaces saturate with respect to N deposition, at least in the case of HNO_3 vapor. In chamber studies, deposition velocity of HNO_3 decreased with increased exposure (Cadle et al., 1991), and washable deposition reached a maximum after 2–4 weeks, whereas continued exposure did not yield any further soluble nitrate (NO_3^-) (Padgett et al., 2004). Little is known about how

dry-deposition fluxes are affected by foliar surface saturation, resuspension of particles, or volatilization of surface-deposited compounds such as ammonium nitrate (NH_4NO_3) during extended rain-free periods. Also unknown is to what degree throughfall may underestimate dry-deposition fluxes when no precipitation occurs for several weeks or months, meaning that no throughfall samples are collected. The fate of compounds deposited to the canopy during prolonged dry periods and methods of quantifying canopy uptake of N and other atmospheric pollutants under such conditions warrant further study.

Throughfall can also be collected under low-lying vegetation such as shrubs or under forest understory vegetation, using trough-style (Bleeker et al., 2003) or miniaturized throughfall resin collectors (Savard, 2005). However, in arid zones, wind-blown dust becomes a problem. For example, throughfall collectors connected to ion exchange resin (IER) columns (see Section 8.3.2) were installed in a desert scrub ecosystem in Joshua Tree National Park, but dust contamination was too severe to allow for throughfall collection. However, miniaturized throughfall resin columns have been used successfully under krummholz in the eastern U.S. (Savard, 2005). Periodic branch rinsing seems to be a more appropriate technique in arid conditions, but this method may overestimate dry-deposition fluxes as described below.

The number of throughfall collectors needed for a particular degree of precision is specific to a given forest site. The number of collectors needed also varies widely depending on the ions being measured. Fewer collectors are needed for deposition than for chemical concentration (mainly because throughfall volumes used to calculate deposition are much less variable than chemical concentrations), and the number needed decreases with longer collection periods (Houle et al., 1999; Lawrence & Fernandez, 1993; Thimonier, 1998). The following formula has frequently been used to calculate the number of collectors to use:

$$n = \frac{t^2 CV^2}{E^2}$$

where n is the number of collectors needed to determine the mean throughfall deposition within a predetermined error and confidence level, t the Student's t value for a given confidence level, CV the coefficient of variation as a percentage, and E the acceptable error (expressed as a percentage of the mean). For example, in a mixed hardwood forest in Quebec, the number of collectors needed to estimate semiannual deposition with a confidence interval of 95% with a 10% error was 13, 14, and 25 for SO_4^{2-} , NO_3^- , and NH_4^+ , respectively (Houle et al., 1999).

Only five collectors were needed to estimate deposition of these same ions with a 20% error. Lawrence and Fernandez (1993) concluded that, for a spruce-fir (*Picea-Abies* spp.) forest in Maine, deposition of most ions on a seasonal or annual basis can be estimated within 20%, a level of precision that is generally adequate, using 20–30 collectors. These rules of thumb are likely to be applicable for plot-level flux estimates or over areas of similar vegetation, topography, and pollution exposure. When vegetation type changes, or with varying topographical features, deposition over the landscape is likely to become more variable (Weathers et al., 2006).

Periodic aqueous rinsing of branches is another simple approach for measuring potential deposition fluxes to vegetation during dry periods. With this method, branches are pre-rinsed at the beginning of the study to remove washable compounds from branch surfaces and to create a starting point for measuring deposition fluxes. Then, at regular intervals (generally every 2 weeks in our studies), the same branches are washed and the rinse solution is collected. This approach is limited to the measurement of ions that do not leach from branches during washing (e.g., NH_4^+ , NO_3^- , and SO_4^{2-}). Alternatively, at the end of the exposure period, the branches can be collected and washed in the laboratory and new branches pre-washed in the field. The foliar surface area of the rinsed branches is measured to calculate deposition fluxes per leaf area. From this information, it is possible to scale up and calculate potential deposition to the larger canopy based on canopy leaf area (Shanley, 1989). However, unless a tower is erected for access throughout the vertical profile of the canopy (Bytnerowicz et al., 1999), it must be assumed that deposition fluxes are similar at all heights. This may not be a problem in ecosystems with open or low-lying canopies such as desert, coastal sage, or subalpine ecosystems. In mixed-species forests, branch-rinsing data and the leaf area for all the major species in the stand are needed. Seasonal deposition fluxes are needed to calculate annual deposition fluxes. If precipitation occurs during an exposure period, the dry-deposition flux cannot be calculated for that time period. The branches must be rinsed again and a new dry-deposition exposure initiated. It can be seen that several critical data parameters are needed to calculate stand-level deposition from branch-rinse flux data and that each one of these parameters entails uncertainty. It should also be remembered that, as with throughfall, retention or uptake of N by branches and foliage might also result in underestimation of total N deposition when using the branch-rinsing method.

In arid or semiarid regions, branch-rinse data may often not be comparable to throughfall deposition data. During periods with infrequent or

no rain for several months, periodic branch rinsing removes a much larger proportion of dry-deposited pollutants than are removed in throughfall (Fenn et al., 2000). Thus, dry-deposition flux data from sequential rinses of the same branches may be more properly considered as a measure of the dry deposition potential. This is because each time branches are washed; a new clean surface is created that is a more effective receptor than a canopy that has not been recently washed, either artificially or by rain. Presumably, dry deposition fluxes are greater to washed than unwashed foliage, which may explain why at two sites in the San Bernardino Mountains over a 7-month period during the dry season (6 months with no precipitation), N deposition fluxes determined from branch rinses were 50% higher than throughfall fluxes (Fenn et al., 2000). These findings suggest that branch-rinse and throughfall data are likely to be more comparable in areas or in seasons when precipitation occurs on a regular basis. In the semiarid San Bernardino Mountains, deposition fluxes to the forest during the 1993 summer dry season, as determined from sequential branch rinses, were comparable to throughfall fluxes measured over the same time period. In this case, it appears that both methods were comparable because periodic low-volume rain events (59 mm precipitation) occurred during the sampling period from late May to mid-November (Fenn & Bytnerowicz, 1997). During extended dry periods, branch rinsing is expected to overestimate throughfall deposition. However, this hypothesis needs further testing.

8.2.3. *Wet deposition and bulk deposition*

Wet deposition measurements refer to deposition in precipitation with dry deposition excluded. The so-called wet/dry bucket collectors [Aerochem Metrics model 301 (Fig. 8.1; Bushnell, Florida) or Loda Electronics model 2001 (Loda, Illinois)] are AC or battery-powered, and are used in the National Atmospheric Deposition Program (NADP) network to collect wet deposition only; a motorized lid covers the collection bucket except during precipitation events. Accurate estimates of wet deposition require efficient collection of precipitation samples and proper handling of samples to prevent degradation of samples before chemical analysis (Krupa, 2002). As far as inorganic N species are concerned, NH_4^+ is particularly susceptible to volatilization or chemical transformation losses during storage. Longer field incubation or sample storage times increase the risk of sample degradation.

A flip-top collector that can collect wet deposition only (or throughfall when placed under a canopy) and does not require electric power to

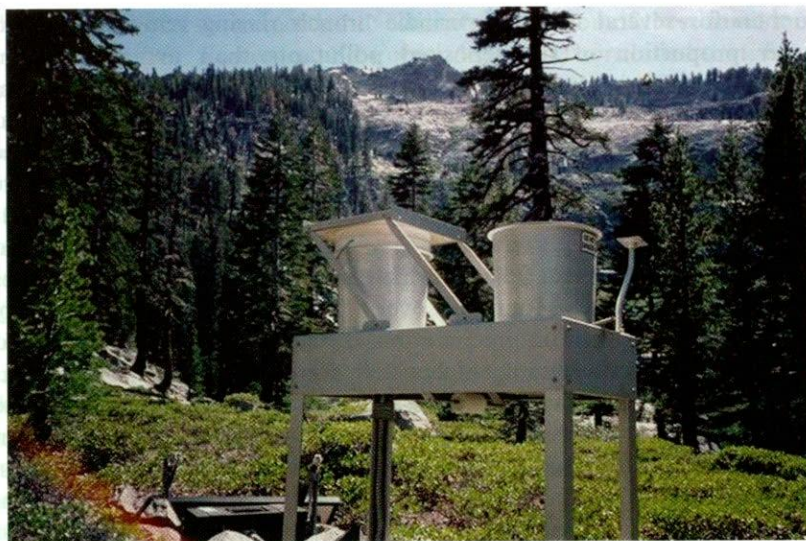


Figure 8.1. Aerochem Metrics model 301 wet/dry bucket collector of the type used in the NADP monitoring network. These collectors are AC or battery powered and are used to collect wet deposition only.

operate is described by Glaubig and Gomez (1994) and Fenn and Bytnerowicz (1997). The lid is held closed over the funnel collector with “magic paper” that rapidly dissolves upon wetting, causing a counter weight to open the lid and allow collection of precipitation or throughfall samples. After the sample solutions are collected, the lid must once again be placed on top of the funnel opening and secured with the dissolvable paper.

In the absence of electric power, deposition in precipitation is usually collected as “bulk deposition,” a term that refers to precipitation samples collected in samplers—often funnels—in which the opening is continuously exposed to the atmosphere, such that some dry-deposited compounds are inevitably collected during intervening dry periods. Throughfall is also usually collected as “bulk throughfall” (Weathers et al., 2001). In European studies, wet-only : bulk deposition ratios for NH_4^+ , NO_3^- , and SO_4^{2-} were frequently 0.75–0.85, although ratios for NH_4^+ and SO_4^{2-} were sometimes as high as 0.96–1.25 (Erisman & Draaijers, 1995). It is not clear why wet deposition of NH_4^+ and SO_4^{2-} was sometimes greater than bulk deposition, but it could be due to error, greater volatilization losses, or microbial assimilation with bulk collectors, or differing collection efficiencies of the wet-only and bulk collectors.

Wet-only: bulk deposition ratios were lower for components such as base cations (Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+}), which deposit as large particles. Similarly, at a montane site in northern Italy, bulk deposition measurements of NH_4^{+} , NO_3^{-} , and SO_4^{2-} were 6–12% higher than wet deposition, but deposition of Ca^{2+} , Mg^{2+} , and K^{+} was 30–50% higher in bulk deposition (Mosello et al., 1988). In arid or semiarid ecosystems, where extended dry periods occur, studies are needed to determine to what extent dry deposition, leaf litter, and insects falling into bulk collectors influence wet deposition measurements.

The largest uncertainty in wet and bulk deposition measurements is the under-collection of precipitation because of air flow distortion caused by the sampler, which results in small droplets following the distorted air flow, thus preventing quantitative capture of rainfall. Under-collection of precipitation worsens with greater wind speed and smaller raindrop diameter (Dämmgen et al., 2005). Some workers have corrected for under-collection of precipitation by using precipitation gauges mounted with the aperture level with the ground and surrounded by an anti-splash grid. Samples for chemical analysis, particularly in arid regions, must still be collected from a height of 1.0–1.5 m to avoid collection of locally resuspended material. Bulk deposition collectors should be replicated at each site in case any collectors are disturbed or to identify samples that are contaminated, for example, with bird droppings. For more details on collection and analysis of wet and bulk deposition samples, see the reviews by Dämmgen et al. (2005) and Krupa (2002). Precipitation occurring as snowfall is particularly difficult to measure accurately because snow is transported horizontally and its sedimentation is slow and because snowfall is frequently associated with highly turbulent crosswinds at ground level (Krupa, 2002). As a result, snowfall is commonly underestimated, although at Niwot Ridge, in the Colorado Front Range, snowfall and associated N deposition were overestimated in wet deposition collectors because of oversampling, resulting from blowing snow events (Williams et al., 1998).

8.2.4. Deposition in cloud water and rime ice

Atmospheric deposition of N in fog or cloud water can constitute more than 35% of total deposition (Anderson et al., 1999), even in arid or semiarid zones where fogs occur as a result of orographic or coastal influences (Fenn & Poth, 2004; Fenn et al., 2000; Waldman et al., 1985; Weathers & Likens 1997; Weathers et al., 2000). Deposition of N and S in fog is an important input in southern California and in the Sierra Nevada

range in central California (Collett et al., 1990). When super-cooled cloud droplets impinge on vegetation or other surfaces, rime ice is formed. Ionic concentrations in rime and cloud water are typically many times higher than in rain or snow. Rime ice can be collected on plastic line or netting-type passive collectors (Berg et al., 1991; Duncan, 1991). In polluted areas, fog or cloud water deposition needs to be accounted for by collecting fog water with active or passive fog samplers (Collett et al., 1990; Fenn et al., 2000; Weathers et al., 1988) or by collecting throughfall. In the latter case, throughfall deposition is an estimate of deposition through fog, precipitation, and dry deposition (Weathers et al., 1992, 1995, 2006). However, in areas of low to moderate N deposition, throughfall fluxes of N can be similar to or less than bulk deposition as a result of canopy uptake of atmospheric N. In such cases, throughfall data cannot be used to estimate inputs of dry and fog deposition. This is particularly true in coastal or other high rainfall areas where canopies are heavily colonized by epiphytic vegetation, which can increase canopy N uptake capacity.

8.2.5. Spatial extrapolation of deposition fluxes

Determining the spatial variation in deposition across a landscape or within a watershed is a key issue for evaluating ecosystem effects of atmospheric deposition (Weathers et al., 2006). For winter deposition in seasonally snow-covered environments, this topic is discussed below in Section 8.5. Recent advances in passive monitoring of atmospheric pollutant concentrations and of deposition in precipitation and throughfall have allowed sufficiently intensive data collection to estimate deposition across selected watersheds. For evaluating deposition over larger regions (e.g., hundreds to thousands of square kilometer), simulation or empirical models (see Section 8.4) are needed, but in the former case, ground verification is still required to evaluate model output.

Total N deposition to forest stands was estimated by Schmitt et al. (2005) with the inferential method using passive monitors to measure gaseous pollutant concentrations, in combination with a regression model for deriving the other terms of the total deposition of N from measurements of bulk N deposition. By implementing a passive monitoring network over the area of interest, it may be possible to estimate dry deposition fluxes of gaseous N compounds across complex terrain such as an entire montane watershed. For total dry N deposition, flux of particulate nitrate and ammonium should also be added. Although theoretically possible, in practice very limited information on

concentrations of these pollutants is available. Such information can be obtained on a small scale from denuder/filter-pack systems, such as in the mixed-conifer forest stand at Barton Flats in the San Bernardino Mountains (Bytnerowicz et al., 1999). In that study, flux from nitrate and ammonium was calculated by the inferential method, multiplying ambient concentrations of nitrate and ammonium in fine particulate matter by literature values of their deposition velocity (Davidson & Wu, 1990). With present technologies, no large-scale evaluation of fine particulate contribution to total dry deposition of N based on field monitoring is possible.

Total deposition can be obtained by adding wet deposition inputs to the estimated dry deposition, although where fog deposition occurs, this must also be measured. Total N deposition can also be estimated from throughfall measurements by calculating the canopy uptake of N using canopy budget models (Draaijers & Erisman, 1995; Schmitt et al., 2005). When using IER throughfall collectors (Section 8.3.2) rather than aqueous samplers, samples do not need to be collected after each event (see Section 8.3.2), and it is now practical to measure throughfall deposition with greater spatial intensity and over much larger land areas (Fenn & Poth, 2004; Simkin et al., 2004). For example, in the Kings River watershed study in the southern Sierra Nevada in California, IER throughfall collectors are being used to measure throughfall deposition in three watersheds with a grid spacing of 150 m throughout the watershed (Hunsaker & Eagan, 2003). A network of passive monitors of gaseous N pollutants has also been established within these watersheds, providing an opportunity to compare N deposition as determined by the inferential (plus wet deposition) and throughfall methods. Both the inferential and throughfall canopy budget model methods entail a high degree of uncertainty in estimating total N deposition, but the use of both methods provides more robust estimates of deposition. Schmitt et al. (2005) found reasonable agreement between the two methods. Bytnerowicz et al. (1999) also found good agreement between summertime estimates of dry deposition in the San Bernardino Mountains using branch rinsing, throughfall, and a quasi-empirical model based on branch-rinse data collected on a tower along the vertical profile of a relatively open, mixed-conifer forest canopy.

For arid systems in particular, the canopy budget models (designed to estimate total N deposition from throughfall data) will likely require adaptation because of the unknown fate of dry-deposited pollutants during long dry periods without canopy wash-off. Furthermore, the canopy models assume little canopy exchange of nitrogen oxides (NO_x), although this is known to be an incorrect assumption (Draaijers & Erisman, 1995).

Canopy exchange may be particularly problematic in western ecosystems exposed to urban photochemical smog, because of the predominance of oxidized forms of N pollutants. Nitric acid vapor is a highly reactive constituent of urban emissions, and controlled exposure studies suggest that 25–50% of the HNO_3 deposited to trees and shrubs native to southern California is not easily washed from foliage. Tracer studies with $^{15}\text{HNO}_3$ indicated that 1–5% of the dry-deposited HNO_3 is absorbed and assimilated into amino acids and proteins by leaves, but a substantially larger portion is retained in a labile form, neither solubilized by water nor isolated from the biologically active pool (Padgett, 2004).

8.2.6. CASTNET, NADP, and IMPROVE monitoring networks

The NADP/National Trends Network (NTN) was established in the late 1970s and has since grown to over 200 monitoring sites in the U.S., and 78 sites in the western U.S. It is the most spatially and temporally extensive atmospheric deposition network in North America. The NADP data have proved invaluable in evaluating spatial and temporal trends in deposition, particularly of pollutants such as inorganic N and S. However, only wet deposition in precipitation is monitored, and thus, the data are of limited usefulness for estimating total deposition inputs, particularly in the montane West where dry deposition, and in some instances fog deposition, constitutes large proportions of total deposition. Other limitations of the NADP network for the western U.S. include low station density, few high-elevation stations, and no measurement of atmospheric organic N loading.

The Clean Air Status and Trends Network (CASTNET) was established in 1987 to collect air chemistry data and model dry deposition inputs to the vegetation near each monitoring station. Currently, there are over 70 monitoring locations, 26 of them in the western states. Weekly average atmospheric concentrations of NH_4^+ , NO_3^- and SO_4^{2-} , SO_2 , and HNO_3 are measured using filter packs, along with hourly concentrations of ambient ozone (O_3) levels and meteorological conditions (<http://www.epa.gov/castnet/>). Filter-pack techniques, although widely used, have been criticized (Pathak & Chan, 2005) because of large errors in determinations of gaseous vs. particulate components of dry deposition (e.g., HNO_3 vs. NO_3^- and NH_3 vs. NH_4^+). Rates of dry deposition are determined at the CASTNET sites with an inferential method using atmospheric concentrations and modeled deposition velocities (Kolian & Haeuber, 2004). Model inputs also include meteorological data and information on land use, vegetation, and surface conditions. Inferential model flux calculations for CASTNET are generally biased low due to the

weekly integrated sampling protocol (Kolian & Haeuber, 2004). Total N deposition is also underestimated because NO, NO₂, NH₃, and organic N are not measured (Baumgardner et al., 2002).

A promising new gas-particle ion-chromatographic system for continuous monitoring of soluble gases and ionic constituents of particulate matter is currently being tested by CASTNET. With this technology, semicontinuous measurements of NH₄⁺ and anions in ambient aerosols and soluble acidic gases and NH₃ can be made with a high degree of robustness and flexibility. This methodology is more expensive than current methods, but if implemented, should improve deposition estimates by providing time-resolved atmospheric concentrations to be used in calculating dry deposition. CASTNET sites are usually co-located with NADP sites, so that total atmospheric inputs can be estimated as the sum of dry and wet deposition. Data from the larger NADP network are frequently used to extrapolate wet deposition over the U.S. However, dry deposition data from CASTNET are mainly considered as an estimate for that monitoring site only, although measurements will often be indicative of relative dry deposition inputs to similar land-cover types in the area, assuming similar pollution exposures.

A comparison of CASTNET dry deposition and total deposition (NADP + CASTNET) with resin throughfall estimates of deposition has been carried out in eastern North America (Weathers, personal communication). These comparisons show that, for this region, throughfall and total deposition compare well over the time period of the summer growing season. Similar comparisons have not been performed on a regional basis in western North America. However, although annual N deposition at Giant Forest in Sequoia National Park was comparatively low, ranging from 2.8 to 3.9 kg ha⁻¹ in 1999, 2001, 2003, and 2004 based on NADP + CASTNET data (<http://www.epa.gov/castnet/sites/sek402.html>), throughfall N deposition at the same site was 11.6 kg ha⁻¹ year⁻¹ (Fenn et al., 2003b). In an earlier study, throughfall deposition was 6.2 and 10.8 kg ha⁻¹ year⁻¹ under nearby mixed fir and Sequoia (*Sequoiadendron giganteum*) stands (Chorover et al., 1994), also much higher than the NADP + CASTNET data. These comparisons indicate that CASTNET + NADP estimates of N deposition in semiarid forests of the West can be several-fold lower than throughfall fluxes. It appears that dry-deposition fluxes of N are grossly underestimated with the CASTNET protocol at Giant Forest for the reasons described earlier and possibly because of high uncertainty in the inferential model (Kolian & Haeuber, 2004). Likewise, deposition in fog, which is important in Sequoia National Park (Collett et al., 1990), is not accounted for in the CASTNET and NADP data.

The Interagency Monitoring of Protected Visual Environments (IMPROVE) network was established in 1985 to measure the key aerosol species affecting visibility in federal Class I areas. Fine particulates NO_2^- , NO_3^- , and SO_4^{2-} are measured, although total atmospheric NO_3^- is probably underestimated because HNO_3 vapor and NO_3^- in the coarse particulate fraction are not measured (Fenn et al., 2003b; <http://vista.cira.colostate.edu/improve/>, last accessed on July 18, 2008). The Speciation Trends Network (STN) is a national network of approximately 1200 PM_{2.5} monitoring sites including samplers that provide mass data, visibility-related measurements, and chemically speciated particulate matter data. The STN database includes data collected from IMPROVE, State, and local air-monitoring stations, and other special study sites. Although the STN and IMPROVE data do not provide direct estimates of deposition, they are useful for validating numerical air quality models that do simulate the deposition of N (<http://www.epa.gov/oar/oaqps/pm25/general.html>, last accessed on December 30, 2008). In summary, although existing monitoring networks provide useful data for characterizing some aspects of N deposition, data from ongoing monitoring networks will generally not provide the data needed to estimate total N deposition or to evaluate spatial and temporal variability in N deposition needed in support of ecosystem effects studies in western North America.

8.2.7. Nitrogen accumulation in surface soils of arid systems

In arid ecosystems, sparse vegetation exposes soil surfaces to direct dry deposition. Padgett et al. (1999) demonstrated that inorganic N accumulates on the surfaces of soils of coastal sage scrub ecosystems in southern California during dry smoggy periods. Nitrogen accumulation was far greater in areas with high levels of atmospheric pollutants. Deposition was also greater in the interspaces between plants than on soil under shrub canopies, which are typically higher in organic N, supporting the argument for an atmospheric source for surface accumulation of inorganic N. Following the onset of the wet season, nitrate concentrations in the top 2 cm of soil rapidly decreased, but could be detected further down the soil profile as N was leached through the soil water profile (Padgett & Bytnerowicz, 2001; Padgett et al., 1999). In controlled HNO_3 fumigation exposures, thin soil layers were found to function as effective N deposition receptors for monitoring HNO_3 deposition fluxes to soil. Deposition velocities of HNO_3 vapor to isolated soil fractions of sand, silt, and clay followed established ion exchange principles of soil chemistry: levels of extractable NO_3^- increased with increasing surface area of the mineral soil particles (Padgett & Bytnerowicz, 2001).

Monitoring of N accumulation in surface soils has also been used in a desert ecosystem in Joshua Tree National Park in southern California for monitoring N deposition to bare soil during the summer drought season (M.E. Fenn, unpublished data).

We have developed a soil plate sampler for estimating deposition fluxes of N to exposed soil. This technique could presumably be used for other pollutants as well. A thin layer of soil is placed in a small dish such as a Petri plate and exposed to the atmosphere for a given time, typically 1 or 2 weeks. In many areas, wind tends to disturb the soil in the plate, making it necessary to fix the soil to a solid surface before field deployment. We found that this can be done effectively by applying a multipurpose aerosol spray adhesive to a plastic disk, over which a thin layer of native soil is spread. The disk is then mounted on a small jar as a lid insert of the style used in glass canning or fruit jars in such a way that the soil disk is exposed to the atmosphere. After the field exposure, nitrate and ammonium (or any other ions of interest) are extracted with 2N KCl and analyzed. Following blank correction, the deposition flux to soil can be calculated.

8.3. Passive monitoring techniques

In general, passive samplers measure long-term (weeks or months) average concentrations of air pollutants. Passive samplers for gaseous pollutants are devices for measuring pollutant concentrations based on passive diffusion of the pollutant through barriers (filters, screens) or diffusion tubes, and onto the collection medium, the latter chosen on the basis of its affinity to the pollutant gas to be sampled. In this section, we will discuss passive samplers that measure time-averaged atmospheric concentrations of key gaseous pollutants and a collector that accumulates ions from precipitation or throughfall solutions using IER methods. Lichens as bio-monitors will also be briefly discussed.

8.3.1. Passive samplers of gaseous pollutants

Krupa and Legge (2000) published a comprehensive review of the use of passive samplers for monitoring ambient air pollution from an ecological effects perspective. In this chapter, we present only selected information on the samplers that have been used in mountain settings. The main advantages of using passive samplers are easy deployment in field conditions, simplicity of design and operation, low requirements for field labor and maintenance, relatively low cost, no need for electric power or

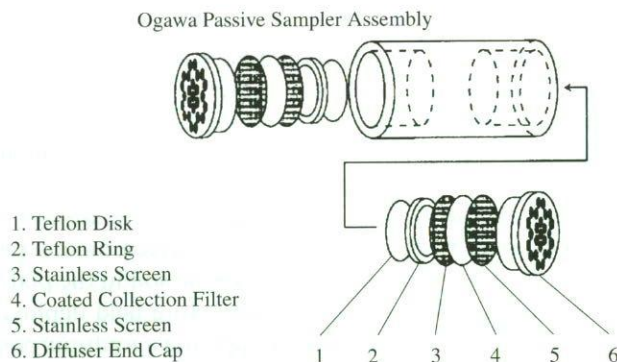


Figure 8.2. Schematic diagram of the Ogawa passive sampler. Depending on the absorbent used on the coated collection filter, these samplers have been used to sample a number of gaseous pollutants including O_3 , NH_3 , NO_2 , NO , NO_x , and SO_2 .

air-conditioned shelters, and feasible use across dense networks allowing for landscape or regional characterization of air pollution distribution patterns. Major disadvantages are low temporal resolution, possible interference from other pollutants, significant effects of meteorological conditions such as wind, temperature, or relative humidity, low detection limits, and poor relationship with vegetation responses (Bytnerowicz *et al.*, 2000; Koutrakis *et al.*, 1993; Krupa & Legge, 2000; Tang, 2001).

Koutrakis *et al.* (1993) designed a passive sampler, now commonly known as the Ogawa passive sampler, which is widely used in North America, Europe, and Asia (Fig. 8.2; <http://www.ogawausa.com/>). The sampler is made of Teflon[®], with a Teflon cap with precision-drilled holes followed by a stainless steel mesh serving as the diffusion barriers. The pollutant to be sampled is collected on cellulose filters that are coated with reagents designed to react with a particular pollutant. Initially, this sampler was used almost exclusively for sampling ambient O_3 on pads coated with sodium nitrite (Alonso *et al.*, 2001; Brace & Peterson, 1998; Bytnerowicz *et al.*, 2001; Fraczek *et al.*, 2003; Gertler *et al.*, 2006; Ray, 2001).

The Ogawa samplers are now also used to determine NH_3 , NO_2 , NO , and SO_2 concentrations (Fig. 8.3). Like earlier sampler designs, NO_2 and SO_2 are collected on filters coated with triethanolamine (TEA), whereas NO_x are collected on filters coated with TEA plus an oxidizing agent (Ogawa, 1998). Ammonia is collected on filters coated with citric acid, resulting in the formation of ammonium citrate $[(NH_4)_2C_6H_6O_7]$, which is extracted from the filters and concentrations of NH_4^+ determined by colorimetric methods (Roadman *et al.*, 2003). Concentrations of NH_3

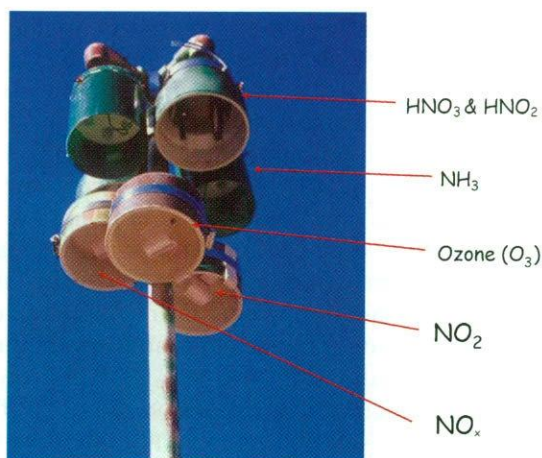


Figure 8.3. Photograph of an array of passive samplers installed for field monitoring of gaseous pollutants. Although not shown, SO₂ is also measured with the Ogawa sampler.

are calculated based on calibrations against reference methods such as annular denuders. Passive samplers for measuring HNO₃ and HNO₂ concentrations (Fig. 8.3) based on quantitative absorption of these gases by nylon filters have been developed by Bytnerowicz et al. (2001, 2005). In the initial sampler design, three nylon filters in PVC rings hang underneath a PVC cap protecting them from rain and wind (Bytnerowicz et al., 2001). A new, improved badge-type HNO₃ sampler uses a Teflon membrane for controlling air-flow to a nylon filter that absorbs HNO₃ (Bytnerowicz et al., 2005).

Passive monitors have been used to characterize air pollution distribution at scales ranging from individual trees to forest stands to mountain ranges or other large-scale applications (Arbaugh & Bytnerowicz, 2003; Bytnerowicz et al., 2004; Gertler et al., 2006; Schmitt et al., 2005). By combining passive sampler data and geostatistical models, large-scale air pollutant exposure patterns can be determined. Such information can point to "hot spots" of air pollutant exposure. For instance, in 1999, approximately 90 O₃ monitoring plots were established in the Sierra Nevada mountain range in California. Measuring O₃ over such a large network revealed some surprising results, such as much higher than expected concentrations during certain meteorological conditions in the "pristine" eastern Sierra Nevada (Fraczek et al., 2003). Similarly, the 2002 study in the Lake Tahoe Basin with about 30 monitoring sites clearly indicated that elevated levels of O₃ and HNO₃ in the Basin resulted mostly

from local emissions, not from long-range transport of polluted air masses from the California Central Valley (Gertler et al., 2006).

Passive samplers are useful for understanding both horizontal and vertical distribution of air pollutants. Brace and Peterson (1998) reported a linear increase in O_3 concentrations with elevation on Mt. Rainier in the Cascades, and Alonso et al. (2003) found that O_3 concentrations in the San Bernardino Mountains in southern California did not change significantly between 1223 and 2667 m elevation. Information gained from passive monitoring networks can guide decisions on where and when active air pollution monitoring equipment should be deployed for understanding distribution of real-time concentrations of air pollutants.

Information on concentrations of NO , NO_2 , NH_3 , HNO_2 , and HNO_3 can also be used to estimate dry deposition of N in forest stands (Bytnerowicz et al., 1999). Atmospheric concentration data from passive samplers can be used to calculate landscape-level N deposition with the inferential method, assuming that additional information such as deposition velocities to various components (trees, understory vegetation, soils, rocks, etc.), LAI, and land-use data are also available (see Section 8.2.1 and Schmitt et al., 2005). Information from passive samplers presented as monthly averages of pollutants can also be used as input for models of air pollution dispersion such as CALPUFF. This is critical for remote areas where real-time air pollution monitoring does not exist.

8.3.2. Throughfall and precipitation monitoring with ion exchange resins

The use of IERs in throughfall and bulk deposition collectors can dramatically reduce the number of trips to field sites, sample numbers, and analysis costs. Fenn and Poth (2004) reported deposition estimates using IER throughfall collectors that compared well with co-located conventional solution collectors for measuring deposition of ammonium and nitrate in throughfall and bulk deposition. The IER collectors functioned well with field deployment times as long as 12 months (the longest time period tested), although IER columns are usually changed out every 6 months. Simkin et al. (2004) showed similar comparisons and utility for sulfate, nitrate, and chloride sampling using IER columns in eastern North America (Fig. 8.4). The IER collector is built of inexpensive materials and is designed and used similarly to conventional throughfall collectors, except that instead of collecting and analyzing the solution on an event or periodic basis, the solution is funneled through an IER column where the anions and cations are reversibly adsorbed on a mixed-bed resin and are collected every 6 weeks to 6 months.

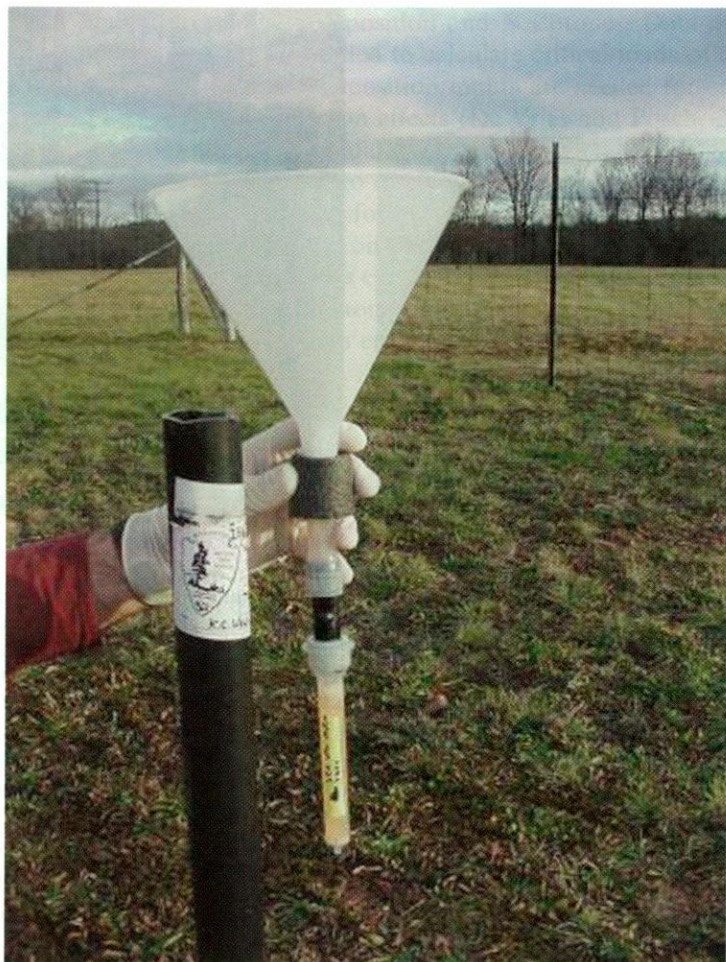


Figure 8.4. A bulk deposition collector using an anion exchange resin column to collect NO_3^- , SO_4^{2-} , and Cl^- in precipitation or throughfall (Simkin et al., 2004). The resin columns are usually exchanged every 6 weeks.

Snow tubes can be attached to the collector funnels (Fig. 8.5) during winter for snow collection, generally at the same time that IER columns are exchanged. Ions in snow are then adsorbed by the IER as the snow melts and percolates through the resin column, although in regions with high snowfall rates other methods must be employed, for example, collecting snow samples, melting them in the laboratory, and passing the solution through resin columns (Weathers et al., unpublished data).



Figure 8.5. A bulk deposition collector using mixed bed (anion and cation) ion exchange resin to collect NH_4^+ , NO_3^- , and SO_4^{2-} in precipitation or throughfall—based on the design described by Fenn and Poeth (2004). The resin columns are usually exchanged after 6 months of field exposure, but in some instances they are changed after 12 months. The collector on the right has a snow tube attached for winter collections.

In sites with extremely low temperatures, for example, boreal forests or subalpine locations, the IERs may lose their effectiveness and should not be used without testing the functionality of the resin under conditions occurring at the field sites. In high-elevation sites with deep or persistent snowpack, the IER collectors are best deployed in late spring or early summer after the bulk of the snowpack has melted; winter deposition can be estimated by sampling the snowpack as described in Section 8.5. At mid- or low-elevation sites, where the use of snow tubes is more appropriate, the collection efficiency of the snow tubes in open areas is expected to be low in many instances (Ranalli et al., 1997; Williams et al., 1998) and to vary temporally and spatially, particularly under windy conditions. Elaborate windshields have been designed to improve snow collection (Hansen & Davies, 2002), but these would not be practical for replicate IER collectors. Snow collection with throughfall collectors is likely to be more efficient under canopies than in open areas because of the sheltering effect of the forest canopy.

The IER collectors can also be used to monitor the deposition of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ and, with the selection of appropriate resins,

possibly to measure organic N deposition and N isotopes. Data on the deposition of base cations are needed to calculate critical loads of deposition for acidity, and N and S deposition inputs are needed for critical loads for acidity and eutrophication effects (De Vries and Posch, 2003). It is anticipated that IER throughfall collectors will play a key role in collecting deposition data needed to calculate critical loads and in determining areas in which critical loads for deposition are exceeded (Weathers et al., 2006). Detailed instructions on the construction of IER collectors and field and laboratory procedures can be found at http://www.fs.fed.us/psw/topics/air_quality/resin_collectors/index.shtml (last accessed on December 30, 2008) and in Simkin et al. (2004).

8.3.3. Lichens as bio-monitors/bio-accumulators of atmospheric deposition

Lichens have been used extensively in western North America as bio-monitors of atmospheric deposition and as early warning signals of adverse ecological effects (Fenn et al., 2003a, 2008; Geiser & Reynolds, 2002). Although lichen monitoring does not provide quantitative total deposition fluxes, lichen data are useful in following spatial and temporal deposition patterns because lichens are good accumulators of pollutants such as N, S, and metals. Lichens have consistent elemental ranges in clean sites, which contrast with pollutant levels in polluted sites. Element analysis thresholds (97.5% quantiles for element concentrations in lichens from background sites) have been developed for lichen species in the Pacific Northwest. These thresholds are used to identify sites with elevated deposition. The relative severity of atmospheric deposition can also be evaluated based on lichen community analyses (<http://www.nacse.org/lichenair/>, last accessed on August 17, 2008). When lichen communities are altered by atmospheric deposition, this is a clear demonstration that ecological effects are already occurring (Fenn et al., 2003a, 2008). Lichen monitoring data are most useful when used in combination with conventional measurements of pollutant concentrations or deposition (Fenn et al., 2007, 2008).

8.4. Simulation modeling of deposition

Models for simulating atmospheric deposition serve useful functions such as providing complete spatial coverage over the modeled domain, simulating long periods with hourly resolution, forecasting future conditions, and simulating the benefits of emissions reductions. However, observations are needed to validate model simulations. Models might be

incomplete and can have compensating errors. Errors sometimes result from poor spatial resolution. Mesoscale models are expensive to operate for long periods and can be "gamed" to get a particular answer. Despite these concerns, atmospheric deposition models combined with observations for validation offer a good approach for quantifying deposition inputs and mechanisms. Models can represent both wet and dry deposition and can simulate deposition through multiple pathways including stomata, cuticle, and ground surfaces.

8.4.1. Empirical deposition modeling over heterogeneous landscapes

Recently, an empirical modeling approach has been developed to estimate deposition across heterogeneous (e.g., montane, coastal, variable land-use/land-cover) landscapes that range in spatial extent from hundreds to thousands of kilometers (Weathers et al., 2000, 2006). The approach quantifies deposition as a function of landscape variables such as elevation, vegetation type, and topographic exposure. It is based on statistical models developed from empirical data and their application within a GIS to create S and N deposition maps. Total deposition (wet + dry + fog) estimates are scaled up from monitoring station data (CASTNET and NADP). This model, the LANDMod, was developed from extensive field data collected from two national parks in the eastern U.S., where elevation and vegetation type were identified as the key variables that controlled deposition over the scale of the parks (250–2500 km²). Resultant maps showed "hot" and "cold" spots of S and N deposition that varied up to 10-fold from regions of high to low deposition. High-elevation conifer forests were predicted to receive the highest deposition and low-elevation open areas (i.e., without forest) the lowest deposition. Validation for the LANDMod showed that it underestimated deposition to high-elevation/high-deposition regions and overestimated for low-elevation/low-deposition regions.

The advantages of this type of empirical modeling and GIS approach are (1) it is based on field data, (2) it uses existing monitoring data to anchor the landscape deposition maps, (3) it is spatially explicit (hot and cold spots can be identified), (4) the approach can be tested in other heterogeneous landscapes, and (5) the modeling results can be updated. It will be especially useful to determine which landscape factors are likely to control deposition in arid and high-elevation western landscapes. We expect that topographic features (e.g., elevation and aspect, LAI, frequency and intensity of fog deposition, as well as snow deposition, accumulation, and redistribution) are likely to be some of the key controlling variables.

8.4.2. Simulation of dry deposition by comprehensive air quality modeling systems

Comprehensive air quality models generally use a three-dimensional (3D) Eulerian grid structure to represent the physical and chemical processes relevant to air quality for scales ranging from local to global. Grid cells can range from about 1 km for local-scale simulations up to several hundred kilometers for hemispheric or global simulations. Input data to these models include emissions inventories for the entire suite of air pollutants, meteorology data generated from numerical weather models, and atmospheric chemistry mechanisms designed to represent the chemical and phase transformations of air pollutants. Dry-deposition fluxes are included in the numerical processing as an important sink for airborne species as well as a model product for use in ecological impact assessments. The surface chemical flux is computed as the product of the chemical concentrations in the lowest model layer and the deposition velocity ($F = V_d C$; Seinfeld & Pandis, 1998). Note that this is a convenient approximation that allows V_d to be parameterized from meteorology and surface characteristics separately from the chemical model. A limitation of this approach is that the surface exchange is assumed to be to the surface only. Bi-directional fluxes, which are important for some chemical species (e.g., NH_3), require chemical difference (DC) across the air-surface interface. Model development efforts are currently underway to add this capability.

The dry-deposition velocity is usually parameterized using an electrical resistance analog where serial and parallel combinations of resistances represent various deposition pathways. There are three primary pathways: (1) to the ground, (2) to the leaf cuticles, and (3) through the stomata into the leaf tissue. Stomatal resistance depends on the degree of stomatal opening, which responds to sunlight as well as water stress (root zone soil moisture) and air temperature and humidity. Stomatal function will also be affected by other biological and environmental stresses, such as disease, parasites, nutrient availability, etc., but these are difficult to incorporate into atmospheric models. Because of similarity between the stomatal pathway for dry deposition and evapo-transpiration, dry-deposition models can be integrated with land surface modeling components of meteorology models. In this way, long-term changes (over weeks and months) in soil moisture and vegetation can be simulated and their effects on dry deposition included (Pleim et al., 2001). In addition to dry deposition, wet deposition from clouds also plays a role in the removal of pollutants. The amount of wet deposition is typically calculated as the integral of the precipitation rate and the cloud water concentration over a certain time interval.

Deposition velocities vary substantially depending on the phase (i.e., gas or aerosol) and chemical species. For example, nitric oxide deposits very slowly but, when oxidized to form HNO_3 , it deposits rapidly, and when HNO_3 condenses with ammonia to form ammonium nitrate aerosol, the deposition rate is reduced for both species. Thus, to simulate the deposition of these species accurately, it is important to represent accurately both the chemical and the phase transformations and to validate the model simulation by comparisons with speciated ambient monitoring data.

One of the more widely used simulation models is the U.S. Environmental Protection Agency's Community Multiscale Air Quality (CMAQ) model. We completed a CMAQ simulation for the calendar year 2002 using a 4-km grid resolution for central and southern California (Tonnesen & Wang, 2005). Meteorology for the simulation was generated using the National Center for Atmospheric Research (NCAR)/Penn State Mesoscale Model (MM5) (Grell et al., 1994), and emissions input data for this simulation were extracted from the Western Regional Air Partnership (WRAP) 2002 emissions datasets. Error and bias in the model performance are relatively large, and this is due in part to large errors in the meteorology and emissions data input to the model. However, errors tend to be smaller for longer averaging periods, and it is likely that errors in the annual simulated N deposition are considerably less than that calculated for hourly or daily averaged PM measurements.

An alternative to 3D Eulerian grid models such as the CMAQ model is the use of Lagrangian models that also treat dry and wet deposition for both gas and aerosol species. Typical users of such models are air quality specialists from government agencies and consultant companies involved in the permit issuing process. In contrast to Eulerian models that simulate the chemistry, transport, and deposition within the 3D grid, Lagrangian models represent puffs of air flowing through the model domain. The spatial distribution of pollutants is approximated by simulating the varying trajectories of multiple puffs. The CALPUFF model (Scire et al., 2000) is a non-steady-state Lagrangian Gaussian puff model containing modules for complex terrain effects, over-water transport, coastal interaction effects, building downwash, wet and dry removal, and simple chemical transformation. It is capable of computing dry-deposition rates of gases and particulates as a function of geophysical parameters, meteorological conditions, and pollutant species through a full resistance model. Similar to the 3D Eulerian models, the surface pollutant deposition flux is calculated as the product of the deposition velocity and the pollutant concentration ($F = V_d C$). The deposition velocity is expressed as the inverse of a sum of "resistances" plus, for particles, gravitational settling terms (Scire et al., 2000). For gases, the "resistances"

include (1) atmospheric resistance, which is determined by the predominant land-use type of each grid cell; (2) deposition layer resistance, which accounts for the molecular diffusion to the transport through the laminar deposition layer; and (3) canopy resistance, which is the resistance for gases in the vegetation layer. The three main pathways for canopy resistance (to the ground, to the leaf cuticles, and through the stomata) are identical to the approach described for Eulerian models earlier. For particulate matter, the resistance in the vegetation layer is not considered as particles are usually assumed to stick to the surface after they penetrate the deposition layer. The deposition velocities for particles are expressed in terms of atmospheric resistance, deposition layer resistance, and a gravitational settling term. In CALPUFF, an empirical scavenging coefficient approach is also included to compute the depletion and wet deposition fluxes due to precipitation scavenging. The primary advantage of Lagrangian models is their simplicity, reduced computational cost, and ability to more directly track the effects of pollutants originating from a particular emissions source. The advantages of Eulerian models include greater physical realism and a more direct representation of the spatial varying patterns of pollutant concentrations and deposition. Because Eulerian models typically include a more complete set of chemical reactions, emissions inventories, and spatial coverage, they are better suited for simulating deposition of air pollutants from many sources and over large regions. However, Eulerian models can exhibit large numerical dispersion and dilution of emissions from a single point source. Lagrangian models may be better suited for simulating deposition from a single, large point source, and for this reason, these models are frequently used to predict pollution exposures downwind from a proposed new emissions source during the permit application process.

8.4.3. Special issues in modeling arid, snow-covered, and mountainous areas

In arid environments, vegetation is sparse and soil moisture is usually very low. This means that the stomatal pathway is usually less important and ground deposition is generally more important. Uptake by dry surfaces is very uncertain and highly variable from one chemical species to the next. Measurements of surface resistances for each chemical species of interest are necessary for realistic parameterizations.

Precipitation events are particularly important in arid ecosystems as many plant species grow and become active only for short periods when water is available. During desert bloom periods, the vegetation cover and activity can increase dramatically. Therefore, the stomatal pathway may become dominant at these times. Thus, the model system must be able

to accurately simulate precipitation events and the resulting growth of vegetation. Most current modeling systems, however, describe vegetation by land-use category and season only. Development of higher resolution land-use data and modeling techniques for desert vegetation are needed for better simulation of dry deposition in arid environments.

Explicit modeling of the snowpack has been added to many mesoscale meteorology models in recent years. Dry-deposition models need to consider deposition to the snowpack. Uptake to snow depends greatly on temperature as melting snow provides an opportunity for dissolution of soluble chemical species. The fraction of melt water can be parameterized by temperature. Deposition models have parallel pathways to ice and liquid water. The liquid water pathway should have a serial resistance representing diffusion through the snowpack.

Mesoscale grid models often have insufficient horizontal grid resolution to accurately represent complex terrain in montane landscapes. A consequence is that ambient boundary layer turbulence is usually underestimated, resulting in underestimated deposition velocities. To improve estimates of dry deposition, sub-grid terrain information can be used to enhance the aerodynamic roughness length. However, unresolved slope effects on the flow fields, particularly canopy infiltration on windward slopes, will not be taken into account. Hence, high-resolution modeling is especially important for modeling in complex terrain.

8.4.4. Comparison of simulated deposition to ground measurements and model evaluation methods

The CMAQ model outputs at the 36-km grid scale identified hotspots of elevated N deposition in the western U.S. (Tonnesen et al., 2003) and performed reasonably well in estimating deposition in the Sierra Nevada and Colorado Front Range where deposition inputs are moderately elevated. Measurements of annual throughfall deposition ranged from 1.4 to 13.4 kg ha⁻¹ at 9 mixed-conifer forest sites along a north-south transect in the Sierra Nevada, compared with simulated deposition of 5–10 kg ha⁻¹ year⁻¹ in the Sierra Nevada (Fenn et al., 2003b). In the Colorado Front Range, deposition ranges from 5 to 8 kg ha⁻¹ year⁻¹ and simulated deposition was 9–10 kg ha⁻¹ year⁻¹.

Simulated deposition (a peak of 11 kg ha⁻¹ year⁻¹ in the Los Angeles Air Basin) was underestimated in the highly polluted western San Bernardino Mountains, where throughfall deposition, including deposition to canopy-free areas of the stand, can be as high as 71 kg ha⁻¹ year⁻¹ (Fenn et al., 2008). The underestimation of N deposition in the San Bernardino Mountains is partially due to the steep N deposition gradients

that are characteristic when dry deposition or fog deposition (i.e., in coastal or montane regions) is a major form of N deposition; a factor generally lost in the 36-km grid scale simulations. In recent 4-km grid simulations for California, simulated N deposition fluxes were approximately $40 \text{ kg ha}^{-1} \text{ year}^{-1}$ in parts of the San Bernardino Mountains (Fig. 8.6), suggesting that modeled deposition values are more realistic in these polluted areas with models run at finer grid resolution. The underestimated deposition in the western San Bernardino Mountains is probably also due to underestimation of deposition in fog, and because NH_3 emissions from dairy farms in the region were not adequately accounted for in the original 36-km CMAQ emissions data. Another N deposition hotspot not picked up in the 36-km simulations is the Phoenix area, where average deposition was estimated to be $13.5 \text{ kg ha}^{-1} \text{ year}^{-1}$, and in the most exposed desert and forested regions located downwind, N deposition was as high as $29 \text{ kg ha}^{-1} \text{ year}^{-1}$. Deposition estimates for the Phoenix area from the 36-km CMAQ simulations were only $6\text{--}7 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Fenn et al., 2003b). Another disadvantage of the 36-km grid

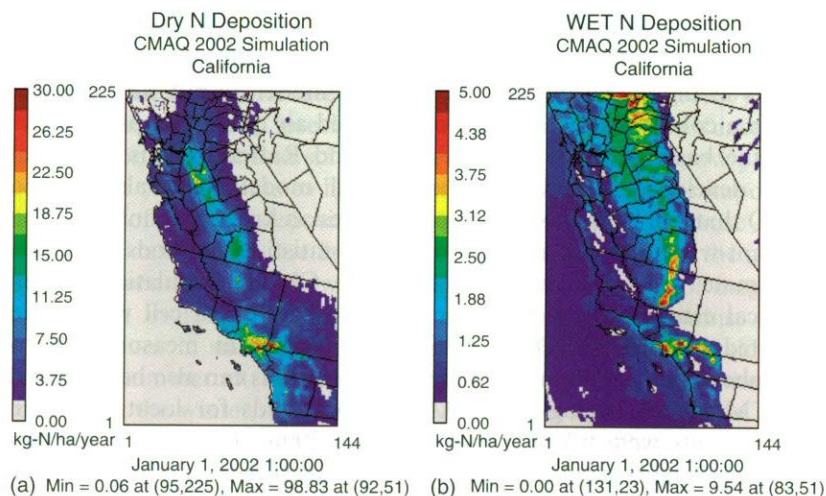


Figure 8.6. Annual dry and wet N deposition in California for the CMAQ air quality model 2002 base case, simulated at a 4-km scale. To best show the variation in deposition over the modeled area, the color scale in the figure was limited to $0\text{--}30 \text{ kg N ha}^{-1} \text{ year}^{-1}$ for dry deposition and $0\text{--}5 \text{ kg N ha}^{-1} \text{ year}^{-1}$ for wet deposition. Actual peak N deposition values were $98.83 \text{ kg ha}^{-1} \text{ year}^{-1}$ for dry deposition in a limited area near Chino Hills in Orange County and ca. $9.54 \text{ kg ha}^{-1} \text{ year}^{-1}$ for wet deposition in montane regions of southern California and in the southern Sierra Nevada in central California.

simulation is that it does not adequately resolve orographic features in montane regions.

Two major problems are encountered when evaluating numerical model output by comparisons with observed data. One is the sparseness of observational data used to compare with model output. The second problem is that observational data and model output are at different spatial resolutions, resulting in the comparison of model-generated grid cell averages with point-referenced monitoring data. The latter problem is known as a "change of support problem" (Fuentes & Raftery, 2005; Swall & Davis, 2006). This problem is acknowledged in comparisons of modeled and monitored deposition fluxes across Europe at the many ICP-forest sites, but comparisons are being made notwithstanding the change of support problem (Simpson et al., 2006). In this case, monitoring data from $30 \times 30 \text{ m}^2$ plots are compared with modeled output for $50 \times 50 \text{ km}^2$ grids. Interpolation or extrapolation methods applied to the point measurements can be used to compare observations to model output, but such comparisons are questionable because of the sparseness of observations and because uncertainty in the interpolated values is not accounted for. Fuentes and Raftery (2005) developed formal Bayesian statistical methods for combining sources of information with different spatial resolutions and for the evaluation of numerical models. The Bayesian methods reported by Fuentes and Raftery (2005) remove the bias in the model output and combine model output with observations in a coherent way, leading to improved air quality maps.

On the basis of the work of Fuentes and Raftery, Davis and Swall (2006) developed a Bayesian hierarchical model for evaluations of CMAQ that can be viewed as a type of Bayesian kriging technique. From the point-wise observed monitoring data, statistical methods were used to estimate the values expected from the CMAQ simulations. These statistical estimates were then compared for each grid cell with values simulated by CMAQ (Davis & Swall, 2006). Point measurements of atmospheric deposition or pollutant concentrations can also be compared with CMAQ by kriging the CMAQ output fields for locations where measurements were taken (Davis & Swall, 2006). However, traditional stationary kriging predictions ignore the uncertainty in the covariance parameters and do not produce appropriate prediction errors (Fuentes & Raftery, 2005). Other statistical approaches have also been used (Fuentes & Raftery, 2005; Mebust et al., 2003), and this is an area of ongoing research. Whereas the aforementioned methods apply to spatial processes at a fixed time point, techniques have also been developed to assess the ability of CMAQ to capture spatiotemporal patterns in pollutant concentrations (Jun & Stein, 2004). In summary, ongoing development of

statistical methods for evaluating numerical models will allow researchers to derive the greatest informational value from observational data and simulation models, while also providing a tool for further improvement of atmospheric simulation models.

8.5. Measuring deposition in high-elevation basins in the Western United States

The hydrology of high-elevation basins in the western U.S. is driven by the accumulation of a seasonal snowpack during winter (usually October–March) and subsequent melting during spring and early summer (usually April–June). Snow generally accounts for most of the precipitation, and the relative importance of snow increases with elevation. In Colorado, for example, snow typically accounts for 50–80% of total precipitation at high-elevation snow monitoring sites in the snowpack telemetry (SNOTEL) program. At Emerald Lake in the Sierra Nevada (elevation 2800 m), snow accounted for 88% of annual precipitation from 1983 to 2000 (Sickman et al., 2001; Sickman and Melack, unpublished data). Summer monsoonal storms typically supply most of the rain in the Rocky Mountains, whereas in the Sierra Nevada, monsoonal rains are less common and most rain derives from low-pressure systems off of the Pacific Ocean during the late autumn (Melack & Sickman, 1997).

Solute deposition in precipitation (wet deposition) is a function of precipitation amount and solute concentration. Although snow provides most of the water inputs to high-elevation basins, its relative importance in terms of solute deposition is less pronounced because solute concentrations in snow are lower than in rain. For example, the average nitrate concentration in snow at Emerald Lake is an order of magnitude lower than in rain. In Loch Vale in the Rocky Mountains, nitrate concentrations in snow are roughly half that in rain. At Emerald Lake, the winter:summer nitrate deposition ratio ranges from 2 to 4, whereas in Loch Vale, the winter:summer nitrate deposition ratio is close to 1.

Total wet deposition is measured at NADP/NTN sites scattered throughout the western U.S., but few of the sites are at high elevation due to difficulties with access and reliable power supplies, as well as restrictions on installation of equipment in wilderness areas (Turk et al., 2001). Data from high-elevation sites often do not meet NADP/NTN quality assurance criteria during winter because the wetfall collectors have a relatively poor capture efficiency for snowfall, especially dry snow that falls during windy conditions. Bulk precipitation collectors, consisting of a continuously open bucket or plastic bag, provide a more reliable

source of data with small investment in equipment and installation (Ranalli et al., 1997).

Snowpack chemistry surveys have been used to fill in data gaps at high elevation for the winter period (Fig. 8.7; Ingersoll et al., 2002; Melack & Sickman, 1997). Total deposition of water and solutes can be accurately determined from snowpack surveys conducted at maximum

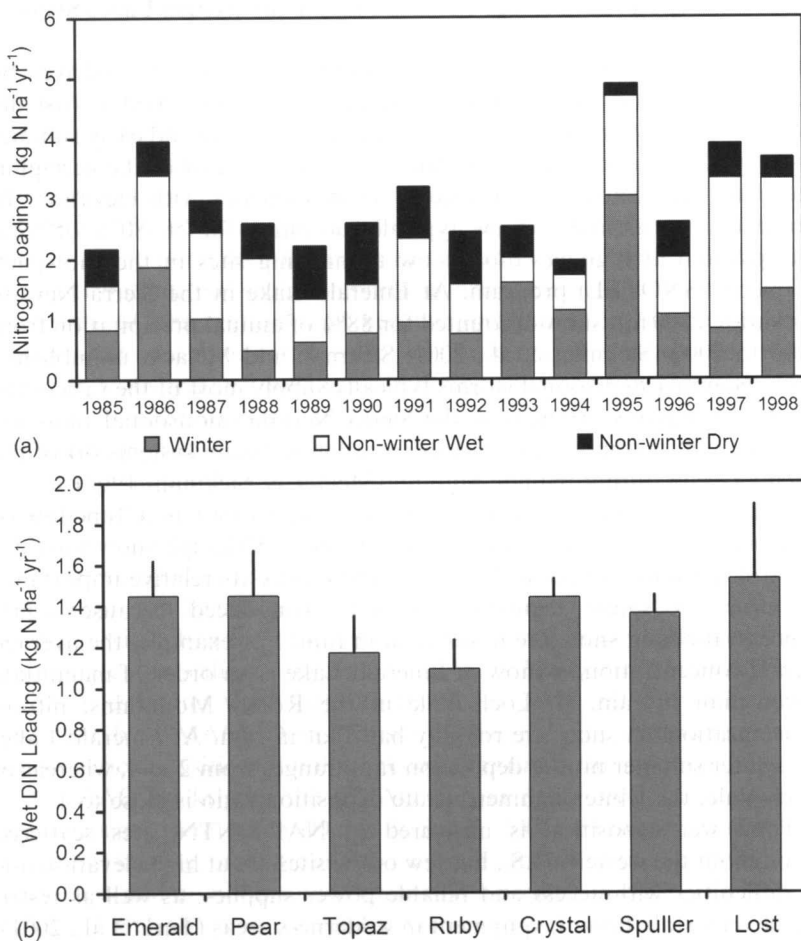


Figure 8.7. Wet, dry, and winter (wet + dry) deposition at Emerald Lake (upper figure) and wet deposition at seven high-elevation sites in the Sierra Nevada, California. Dry deposition was determined by the inferential method and wet deposition with precipitation collectors. Winter deposition (wet + dry) was determined by sampling the accumulated snow pack in spring.

accumulation, typically on or near 1 April. Owing to relatively little or no winter snowmelt above ca. 2500 m (Leydecker & Melack, 1999), total winter deposition of solutes can be estimated with high accuracy (Berg et al., 1989). In addition, because the snow surface is an efficient scavenger of atmospheric aerosols and particles, total wet + dry deposition of most elements can be estimated with a single, integrated sample of the spring snowpack (Sickman et al., 2001).

New types of passive collectors (IER bulk deposition collectors; Section 8.3.2) hold promise for filling data gaps for dry deposition during the summer period (Fenn & Poth, 2004). Snow surveys and passive collectors sample a combination of wet and dry deposition, often referred to as "bulk deposition." When installed in forested areas, passive collectors may also be installed below the canopy to sample "through-fall," which reflects total deposition to vegetation. Dry deposition can contribute a significant fraction of total deposition, especially in mountainous areas that receive relatively little summer rain (Fig. 8.7). Approximately one-third of annual N and S deposition can occur as summer dry deposition in drought years in the Sierra Nevada (Sickman et al., 2001) and Rocky Mountains (Campbell et al., 2000).

On an annual basis, temporal and spatial variability of wet deposition of N, S, and other solutes is primarily a function of variations in precipitation quantity; variations in chemical concentration explain a lesser amount of depositional variation (Lovett, 1994; Naftz et al., 1994). For example, over the past two decades, non-winter rainfall and winter snowfall at the Emerald Lake watershed have varied by factors of 16.4 and 4.6, respectively. In contrast, annual volume-weighted mean NO_3^- and SO_4^{2-} concentrations varied by only 3- to 4-fold during the same period. Similarly, during any year, variations in snow water equivalence among catchments are typically greater than catchment-to-catchment variability of snow chemistry. For example, snow water equivalence ranged from 1200 to over 3000 mm among 15 Sierra Nevada watersheds during 1992–1993, whereas mean snowpack N concentrations varied only from 1.6 to 2.3 $\mu\text{Eq L}^{-1}$ at these same sites (Sickman et al., 2001).

8.5.1. Snow sampling methods

Estimating solute deposition in snow involves collecting snow samples for measurement of solute concentration, and multiplying those concentrations by the snowpack water content, which can be manually measured or estimated from remote sensing data. Snow samples may be collected using either the coring method (Campbell et al., 2000) or the snowpit method (Figs. 8.8 and 8.9; Ingersoll et al., 2002; Naftz et al., 2002).



Figure 8.8. A snowpit dug for collecting snow samples.

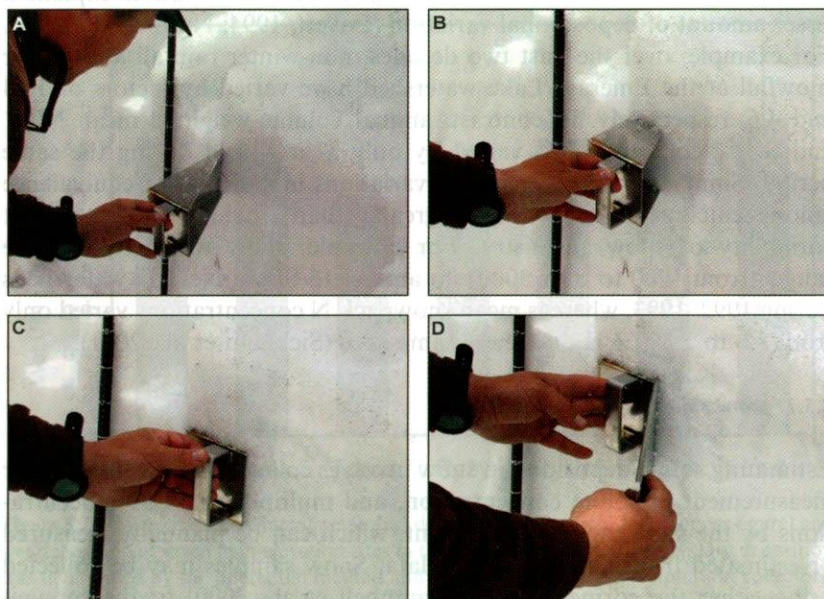


Figure 8.9. Sampling snow from the side of a snowpit. Photos courtesy of K. Elder.

In either case, it is critical to sample the snowpack before the initiation of snowmelt because of preferential loss of solutes during the first phase of melting (Berg, 1992; Harrington & Bales, 1998). Careful attention also must be paid to proper cleaning of sampling equipment and use of ultra-clean sampling techniques due to the very dilute nature of snow (Ingersoll et al., 2002). Strong acids and detergents should be avoided in the cleaning procedure, which primarily consists of soaking apparatus in 18 M Ω de-ionized water for several days. The QA/QC should include an adequate number of blanks (field and lab) and replicates to ensure that contamination was avoided. The methods described later are pertinent to collection for analysis of major solute chemistry (see references for detailed descriptions of methods).

The snow-coring method of snow sampling involves pushing a clean snow-coring device vertically into the snowpack until just above the ground, then pulling the device and (hopefully) the snow core out of the snowpack. Samples are then poured out of the top of the coring device, and into clean plastic or Teflon bags. Bagged samples are then frozen until processed for analysis. Snow samples are generally filtered through 0.45- μ m membrane filters (polycarbonate) into bottles that have been soaked in de-ionized water; glass fiber filters should be avoided as they leach cations into solution (see Melack and Sickman, 1997; Ingersoll et al., 2002, for processing and analysis methods). A Federal Sampler can be used as the coring device as long the inside of the sampler has not been treated with chemicals or wax, which is sometimes used to prevent snow from sticking to the inside of the device. One advantage of using a Federal Sampler as the coring device is that it is designed to measure snowpack water content, permitting calculation of total deposition. Although the snow-coring method is simple and fast, it has the disadvantage that contamination by soil, vegetation, and even the coring device is more difficult to avoid than when using the snowpit method. The Federal Sampler is not appropriate for trace metal sampling because it is made of aluminum. Other disadvantages of the snow-coring method are that it provides no information on whether the snowpack has started melting, and deep snowpacks can be extremely difficult to sample because of ice lenses and dense snow that cause under-sampling.

The snowpit method of snow sampling involves digging a snowpit from the top of the snow surface to the ground (Fig. 8.8). The face of the pit that faces away from the sun is then shaved back using a clean plastic shovel. A depth-integrated snow sample is extracted from one wall of the pit, avoiding the top and bottom 10 cm of the snowpack to prevent contamination. Tools to perform the actual sampling may include clean plastic shovels, such as those designed for avalanche safety, or clear 2-in

PVC pipe. The shovel technique has been extensively tested and used for many years in the annual Rocky Mountain Snowpack Survey and by researchers in the Sierra Nevada (Ingersoll et al., 2002; Sickman et al., 2001). Samples extracted from the pit wall are placed in clean high-density polyethylene or Teflon bags and then frozen until processed for analysis. Snowpack temperatures typically are measured every 10 or 20 cm to verify that the snowpack has not begun to melt. Snow density is also measured at regular intervals (e.g., 10 or 20 cm) to allow calculation of total snowpack water content and subsequently total solute deposition.

The snowpit method can be modified slightly to allow collection of large-volume samples for analysis of S or N isotopic composition (Mast et al., 2001) or pesticides and organic contaminants (Landers et al., 2003). Isotopic tracers provide a very useful technique for determining the sources of NO_3^- and SO_4^{2-} in environmental solutes (Kendall & McDonnell, 1998; Kester et al., 2003). These methods are often used to ascertain the proportion of NO_3^- or SO_4^{2-} in solution or in runoff that comes from atmospheric deposition and from nutrient cycling sources (e.g., nitrification). Nitrate has commonly been traced using the dual isotope technique in which the ^{15}N and ^{18}O signal of NO_3^- are measured in the major NO_3^- sources and in watershed runoff samples. More recently, the $\Delta^{17}\text{O}$ signal of NO_3^- has been used to trace atmospheric NO_3^- and was found to be a more robust tracer of atmospheric NO_3^- (Michalski et al., 2004) than ^{15}N and ^{18}O methods. As with nitrate, multiple isotopic techniques exist to examine S sources in atmospheric deposition, and biogeochemical processes involving S in watersheds. Measurements of stable isotopes of S and O of SO_x have been employed to apportion atmospheric deposition sources (Mast et al., 2001; Mcardle & Liss, 1995; Wadleigh et al., 1996). Radioactive ^{35}S is the most abundant and longest lived of the radioisotopes of S with a half-life of 87 days. The isotope's primary advantage is that it allows a direct determination of the amount of the present year's sulfate deposition in surface and groundwater (Michel et al., 2002); older sources of sulfate, whether derived from biogeochemical processes in catchment soils or prior year's atmospheric deposition, have no ^{35}S . Combining stable and radioisotope measurements of sulfate in catchment studies can provide considerable information regarding the sources and fate of atmospherically deposited S (Kester et al., 2003).

8.5.2. Spatial distribution of snow water equivalent

Because of the strong relationship between snowpack accumulation and atmospheric deposition rates in high-elevation systems, determination of deposition amounts over the landscape requires quantification of

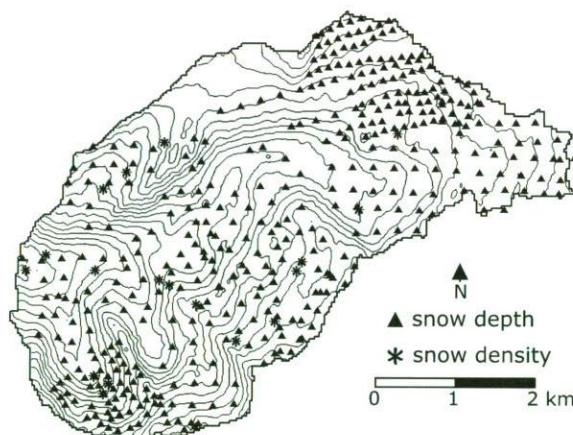


Figure 8.10. Distribution of point measurements of snow depth and density within the Tokopah Basin located in the alpine region of Sequoia National Park, California. Reproduced from Molotch et al. (2005). Copyright 2004, with permission from John Wiley & Sons Limited.

snowpack or snow water equivalent (SWE). A simple average of spatially distributed observations of snow depth and snow density (Fig. 8.10) can provide a good approximation of basin mean SWE (Cline et al., 1998); however, in many applications, the spatial distribution of SWE is needed as feedbacks with the nitrogen cycle occur spatially. Spatial estimates of SWE have been obtained using statistical interpolation of point measurements (Elder et al., 1998) and using remote sensing data (Carroll & Vadnais, 1980; Chang et al., 1991). The methods used in any particular application largely depend on the scale of the application and the available data within the study region. Given the physiographic heterogeneity of mountainous landscapes, statistical models are limited by a lack of ground-based data for the development of interpolation algorithms that are transferable over regional scales. Similarly, remotely sensed SWE data are limited in mountainous terrain due to the coarse resolution of the available data (e.g., 25 km^2) relative to the sub-pixel physiographic heterogeneity of mountainous landscapes. A discussion of remote sensing techniques for measuring SWE is beyond the scope of this chapter, as these techniques have not proved particularly useful in complex rugged terrain. For a review of SWE measurement techniques from satellite and aircraft, the reader is referred to König et al. (2001) and Carroll and Vose (1984).

Significant progress toward realizing relationships between snow accumulation and physiographic variables has been made where detailed snowpack measurements are available (Fig. 8.11; Balk & Elder, 2000; Elder, 1995; Elder et al., 1995, 1998; Erxleben et al., 2002; Molotch et al.,

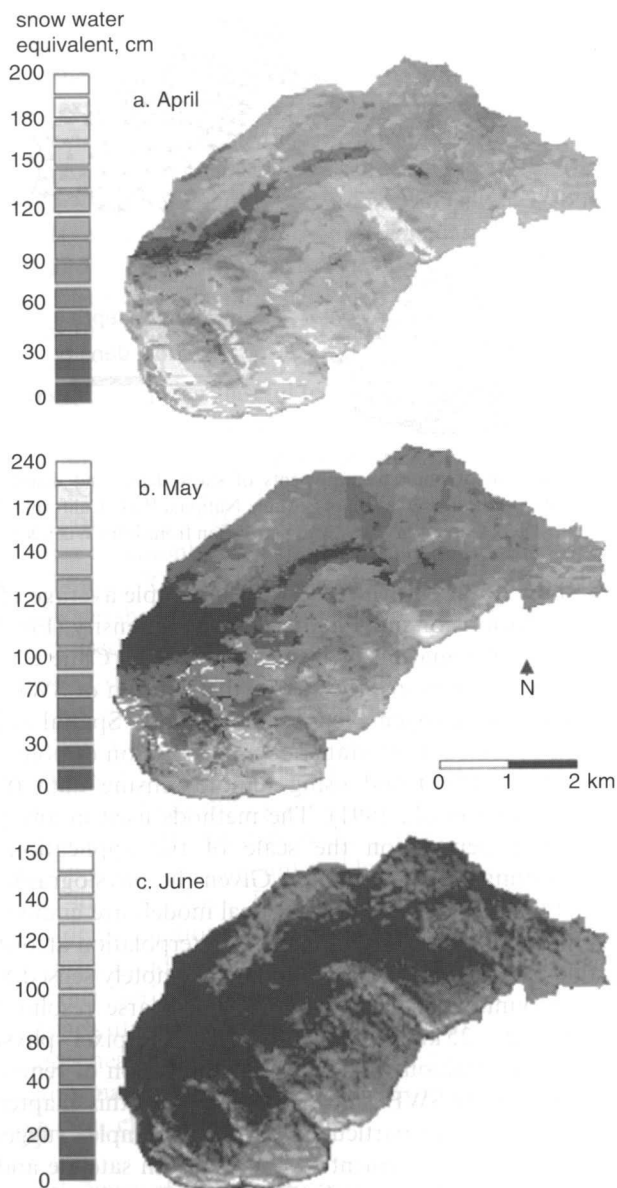


Figure 8.11. Simulated snow water equivalent in the Tokopah Basin (Sequoia national park) in April, May, and June 1997. Reproduced from Molotch et al. (2005). Copyright 2004, with permission from John Wiley & Sons Limited.

2005; Winstral et al., 2002). When these relationships are statistically significant, binary regression trees (Breiman et al., 1984) have proven to provide the most accurate spatial estimates of SWE (Erxleben et al., 2002). The most commonly used independent variables in these models are net solar radiation, slope, elevation, and in some cases, vegetation type. Improvements have been obtained by including additional independent variables representing wind redistribution of snow (Molotch et al., 2004b; Winstral et al., 2002) and aspect (Erxleben et al., 2002).

At the regional scale, or in situations where detailed snowpack observations are not available, statistical interpolation of SNOTEL data is the most widely used technique to estimate the spatial distribution of SWE (Carroll & Carroll, 1993; Carroll & Cressie, 1996; Daly et al., 2000; Fassnacht et al., 2003; Ling et al., 1996; Molotch et al., 2004a). Energy and mass balance models are used by the National Operational Hydrologic Remote Sensing Center (NOHRSC) to estimate SWE across the U.S. (Carroll et al., 2001). In addition to a suite of model forcings, the NOHRSC model requires SWE observations made at SNOTEL sites to update model state variables. The purpose of the SNOTEL network is to provide information for runoff forecasting using empirical relationships between point values of SWE and observed runoff and, therefore, may not provide representative measurements for these spatial applications (Molotch & Bales, 2005).

The recent modeling efforts of Nanus et al. (2003) are an excellent example of integration of multiple datasets to assess spatial patterns in atmospheric deposition. Similar work is underway in the eastern U.S. (Weathers, personal communication) and has been published for parts of the U.S. and Europe (Holland et al., 2005). In these studies, precipitation quantity maps were combined with spatially modeled precipitation chemistry to produce deposition maps of N and S for the entire regions. In the work by Nanus et al. (2003), deposition maps were produced for the Rocky Mountain region at a 1-km resolution. Maps of precipitation amounts were created by the Parameter-Elevation Regressions on Independent Slopes (PRISM) model. The model used various precipitation data sets spatially interpolated with a digital elevation model (Daly et al., 2000). Precipitation chemistry was not well correlated to elevation or other terrain variable, so a simple spatial kriging model was used that incorporated both NADP/NTN and snowpack chemical concentrations measured during surveys. Snowpack concentrations were adjusted to annual concentrations by modeling annual vs. snow accumulation season concentrations (Nanus et al., 2003). The deposition maps produced for the Rocky Mountains are an example of creative use of available data on precipitation and wet deposition chemistry. The major

limitations of the deposition maps produced by Nanus et al. (2003) are that NH_4^+ deposition and dry deposition were not included in the analysis. A slight bias for higher concentrations of NH_4^+ in bulk vs. wet deposition suggests a significant contribution from winter dry deposition of NH_4^+ (Clow et al., 2002). However, for sulfate and nitrate, co-located snowpack and wetfall measurements have shown little contribution from dry deposition during the winter months in the Rocky Mountains (Clow et al., 2002). The overall approach used by Nanus et al. (2003) can be improved by addition of NH_4^+ and organic nitrogen and by using additional spatial interpolation techniques and data at finer spatial scales.

All the techniques described earlier—and future techniques using remote sensing—rely, to some degree, on ground-based rainfall and SWE observations to update model state or to evaluate precipitation estimates. Hence, the inability to scale point observations to the resolution of remotely sensed data and/or model grid elements is one of the most pressing issues for estimating rainfall and SWE distribution at the regional scale or in inaccessible mountainous regions of the western U.S.

8.6. Conclusions

Innovations in passive monitoring methods for measuring atmospheric pollutant concentrations and deposition inputs in throughfall and bulk deposition have increased our capacity to quantify deposition inputs and variability across the landscape. More studies are needed on methods of estimating total N deposition from throughfall deposition fluxes, particularly in arid zones. Improved atmospheric deposition simulation models and techniques for determining real-time concentrations of gaseous and particulate pollutants are also expected to lead to improved estimates of dry-deposition inputs. Because of the difficulty in accurately measuring dry-deposition inputs to complex landscapes in western North America, the implementation of more than one method is often recommended. Furthermore, the deposition monitoring methods to be used in each situation vary greatly based on spatial scale, climatological conditions, topography, the physical and chemical forms of atmospheric deposition, and vegetative cover properties.

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REFERENCES

- Alonso, R., Bytnerowicz, A., and Arbaugh, M. 2001. Vertical distribution of ozone and nitrogenous pollutants in an air quality Class I area, the San Geronio Wilderness, southern California. *ScientificWorld* 1, 10–26.
- Alonso, R., Arbaugh, M.J., and Bytnerowicz, A. 2003. Forest health research on a natural air pollution gradient in the San Bernardino Mountains, southern California. *Ekologia* (Bratislava) 22, 18–23.
- Anderson, J.B., Baumgardner, R.E., Mohnen, V.A., and Bowser, J.J. 1999. Cloud chemistry in the eastern United States, as sampled from three high-elevation sites along the Appalachian Mountains. *Atmos. Environ.* 33, 5105–5114.
- Arbaugh, M.J., and Bytnerowicz, A. 2003. Introduction to a regional passive ozone sampler network. In: Bytnerowicz, A., Arbaugh, M.J., and Alonso, R., eds. *Developments in environmental science, Volume 2: Ozone air pollution in the Sierra Nevada: Distribution and effects on forests*. Elsevier, Amsterdam, The Netherlands, pp. 157–164.
- Balk, B., and Elder, K. 2000. Combining binary decision tree and geostatistical methods to estimate snow distribution in a mountain watershed. *Water Resour. Res.* 36, 13–26.
- Baumgardner, R.E., Lavery, T.F., Rogers, C.M., and Isil, S.S. 2002. Estimates of the atmospheric deposition of sulfur and nitrogen species: Clean Air Status and Trends Network, 1990–2000. *Environ. Sci. Technol.* 36, 2614–2629.
- Berg, N., Marks, D., Dawson, D., McGurk, B., Melack, J., Setaro, F., and Bergman, J. 1989. Evaluation of methods for measurement of snowfall and collection of snow for chemical analysis. Final Report, Contract A6-078-32. California Air Resources Board, Sacramento, CA, USA.
- Berg, N., Dunn, P., and Fenn, M. 1991. Spatial and temporal variability of rime ice and snow chemistry at five sites in California. *Atmos. Environ.* 25A, 915–926.
- Berg, N.H. 1992. Ion elution and release sequence from deep snowpacks in the central Sierra Nevada, California. *Water Air Soil Pollut.* 61, 139–168.
- Bleeker, A., Draaijers, G., van der Veen, D., Erisman, J.W., Mols, H., Fonteijn, P., and Geusebroek, M. 2003. Field intercomparison of throughfall measurements performed within the framework of the Pan European intensive monitoring program of EU/ICP Forest. *Environ. Pollut.* 125, 123–138.
- Brace, S., and Peterson, D.L. 1998. Spatial patterns of tropospheric ozone in the Mount Rainie region of the Cascade Mountains. *Atmos. Environ.* 32, 3629–3637.
- Breiman, L., Friedman, J., Olshen, R., and Stone, C. 1984. *Classification and Regression Trees*. Wadsworth and Brooks, Pacific Grove, CA.
- Bytnerowicz, A., Fenn, M.E., Miller, P.R., and Arbaugh, M.J. 1999. Wet and dry pollutant deposition to the mixed conifer forest. In: Miller, P.R., and McBride, J.R., eds. *Oxidant air pollution impacts in the montane forests of southern California: A case study of the San Bernardino Mountains*, Ecological Studies 134. Springer, New York, pp. 235–269.
- Bytnerowicz, A., Carroll, J.J., Takemoto, B.K., Miller, P.R., Fenn, M.E., and Musselman, R.C. 2000. Distribution and transport of air pollutants to vulnerable California ecosystems. In: Scow, K.M., Fogg, G.E., Hinton, D.E., and Johnson, M.L., eds. *Integrated assessment of ecosystem health*. Lewis Publishers, Boca Raton, FL, pp. 93–118.
- Bytnerowicz, A., Padgett, P.E., Arbaugh, M.J., Parker, D.R., and Jones, D.P. 2001. Passive sampler for measurements of atmospheric nitric acid vapor (HNO_3) concentrations. *ScientificWorld* 1, 815–822.
- Bytnerowicz, A., Arbaugh, M.J., Padgett, P.E., Alonso, R., Fraczek, W., Takemoto, B., Procter, T., Pronos, J., Reiner, J., and Ahuja, S. 2004. Evaluation of ozone and

- HNO₃ vapor distribution and ozone effects on conifer forests in the lake Tahoe Basin and Eastern Sierra Nevada. Final Report to the California Air Resources Board, Sacramento, CA, USA.
- Bytnerowicz, A., Sanz, M.J., Arbaugh, M.J., Padgett, P.E., Jones, D.P., and Davila, A. 2005. Passive sampler for monitoring ambient nitric acid (HNO₃) and nitrous acid (HNO₂) concentrations. *Atmos. Environ.* 39, 2655–2660.
- Cadle, S.H., Marshall, J.D., and Mulawa, P.A. 1991. A laboratory investigation of the routes of HNO₃ dry deposition to coniferous seedlings. *Environ. Pollut.* 72, 287–305.
- Campbell, D.H., Baron, J.S., Tonnessen, K.A., Brooks, P.D., and Schuster, P.F. 2000. Controls on nitrogen flux in alpine/subalpine watersheds of Colorado. *Water Resour. Res.* 36, 37–47.
- Carroll, S., and Cressie, N. 1996. A comparison of geostatistical methodologies used to estimate snow water equivalent. *Water Resour. Bull.* 32, 267–278.
- Carroll, T., and Vadnais, K. 1980. Operational airborne measurement of snow water equivalent using natural terrestrial gamma radiation. *Proceedings of the Western Snow Conference*, vol. 48, pp. 97–106.
- Carroll, T., and Vose, G.D. 1984. Airborne snow water equivalent measurements over a forested environment using terrestrial gamma radiation. *Proceedings of the Eastern Snow Conference*, vol. 29, pp. 101–115.
- Carroll, T., and Carroll, T.R. 1993. Increasing the precision of snow water equivalent estimates obtained from spatial modeling of airborne and ground-based snow data. *Proceedings of the Eastern Snow Conference*, vol. 50, pp. 83–87.
- Carroll, T.R., Cline, D., Fall, G., Nilsson, A., Li, L., and Rost, A. 2001. NOHRSC operations and the simulation of snow cover properties for the coterminous U.S. *Proceedings of the Western Snow Conference*, vol. 69, pp. 1–14.
- Chang, A.T.C., Foster, J.L., and Rango, A. 1991. Utilization of surface cover composition to improve the microwave determination of snow water equivalent in a mountain basin. *Int. J. Remote Sens.* 12, 2311–2319.
- Chorover, J., Vitousek, P.M., Everson, D.A., Esperanza, A.M., and Turner, D. 1994. Solution chemistry profiles of mixed-conifer forests before and after fire. *Biogeochemistry* 26, 115–144.
- Cline, D.W., Bales, R.C., and Dozier, J. 1998. Estimating the spatial distribution of snow in mountain basins using remote sensing and energy balance modeling. *Water Resour. Res.* 34, 1275–1285.
- Clow, D.W., Ingersoll, G.P., Mast, M.A., Turk, J.T., and Campbell, D.H. 2002. Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: Implications for winter dry deposition. *Atmos. Environ.* 36, 2337–2348.
- Collett, J.L., Jr., Daube, B.C., Jr., and Hoffmann, M.R. 1990. The chemical composition of intercepted cloudwater in the Sierra Nevada. *Atmos. Environ.* 24A, 959–972.
- Daly, S.F., Davis, R., Ochs, E., and Pangburn, T. 2000. An approach to spatially distributed snow modeling of the Sacramento and San Joaquin basins, California. *Hydrologic. Proc.* 14, 3257–3271.
- Dämmgen, U., Erisman, J.W., Cape, J.N., Grünhage, L., and Fowler, D. 2005. Practical considerations for addressing uncertainties in monitoring bulk deposition. *Environ. Pollut.* 134, 535–548.
- Davidson, C.I., and Wu, Y.-I. 1990. Dry deposition of particles and vapors. In: Lindberg, A.S., Page, E.L., and Norton, S.A., eds. *Acidic precipitation*, vol. 3. Sources deposition and canopy interactions. Springer, New York.
- Davis, J.M., and Swall, J.L. 2006. An examination of the CMAQ simulations of the wet deposition of ammonium from a Bayesian perspective. *Atmos. Environ.* 40, 4562–4573.

- De Vries, W., and Posch, M. 2003. Critical levels and critical loads as a tool for air quality management. In: Hewitt, C.N., and Jackson, A.V., eds. *Handbook of atmospheric science: Principles and applications*. Blackwell Science Publishing, Oxford, UK, pp. 562–602.
- Draaijers, G.P.J., and Erisman, J.W. 1995. A canopy budget model to assess atmospheric deposition from throughfall measurements. *Water Air Soil Pollut.* 85, 2253–2258.
- Duncan, L.C. 1991. Chemistry of rime and snow collected at a site in the Central Washington Cascades. *Environ. Sci. Technol.* 26, 61–66.
- Elder, K. 1995. Snow distribution in alpine watersheds. PhD dissertation. University of California, Santa Barbara, CA, 309 pp.
- Elder, K., Michaelsen, J., and Dozier, J. 1995. Small basin modeling of snow water equivalence using binary regression tree methods. In: Tonnessen, K. A., Williams, M.W., and Trantor, M., eds. *Biogeochemistry of seasonally snow-covered catchments*. IAHS Publication, Wallingford, CO, 228, 129–139.
- Elder, K., Rosenthal, W., and Davis, R.E. 1998. Estimating the spatial distribution of snow water equivalence in a montane watershed. *Hydrologic. Proc.* 12, 1793–1808.
- Erisman, J.W., and Draaijers, G.P.J. 1995. Atmospheric deposition in relation to acidification and eutrophication. *Studies in environmental science* 63. Elsevier, Amsterdam, The Netherlands.
- Erisman, J.W., Beier, C., Draaijers, G., and Lindberg, S. 1994. Review of deposition monitoring methods. *Tellus* 46B, 79–93.
- Erxleben, J., Elder, K., and Davis, R. 2002. Comparison of spatial interpolation methods for estimating snow distribution in the Colorado Rocky Mountains. *Hydrologic. Proc.* 16, 3627–3649.
- Fassnacht, S.R., Dressler, K.A., and Bales, R.C. 2003. Snow water equivalent interpolation for the Colorado River Basin from snow telemetry (SNOTEL) data. *Water Resour. Res.* 39, doi:10.1029/2002WR001512.
- Fenn, M.E., and Bytnerowicz, A. 1997. Summer throughfall and winter deposition in the San Bernardino Mountains in southern California. *Atmos. Environ.* 31, 673–683.
- Fenn, M.E., and Poth, M.A. 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: A field test in the San Bernardino Mountains. *J. Environ. Qual.* 33, 2007–2014.
- Fenn, M.E., Poth, M.A., Schilling, S.L., and Grainger, D.B. 2000. Throughfall and fog deposition of nitrogen and sulfur at an N-limited and N-saturated site in the San Bernardino Mountains, southern California. *Can. J. Res.* 30, 1476–1488.
- Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W., and Neitlich, P. 2003a. Ecological effects of nitrogen deposition in the western United States. *BioScience* 53, 404–420.
- Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., and Sickman, J.O. 2003b. Nitrogen emissions, deposition, and monitoring in the western United States. *BioScience* 53, 391–403.
- Fenn, M.E., Geiser, L., Bachman, R., Blubaugh, T.J., and Bytnerowicz, A. 2007. Atmospheric deposition inputs and effects on lichen chemistry and indicator species in the Columbia River Gorge, USA. *Environ. Pollut.* 146, 77–91.
- Fenn, M.E., Jovan, S., Yuan, F., Geiser, L., Meixner, T., and Gimeno, B.S. 2008. Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests. *Environ. Pollut.* 155, 492–511.
- Fraczek, W., Bytnerowicz, A., and Arbaugh, M.J. 2003. Use of geostatistics to estimate surface ozone patterns. In: Bytnerowicz, A., Arbaugh, M.J., and Alonso, R., eds. *Ozone*

- air pollution in the Sierra Nevada: Distribution and effects on forests. *Developments in environmental science* 2. Elsevier, Amsterdam, The Netherlands, pp. 215–247.
- Fuentes, M., and Raftery, A.E. 2005. Model evaluation and spatial interpolation by Bayesian combination of observations with outputs from numerical models. *Biometrics* 61, 36–45.
- Geiser, L., and Reynolds, R. 2002. Using lichens as indicators of air quality on federal lands. Workshop Report. USDA Forest Service, PNW Region, R6-NR-AG-TP-01-02. <http://ocid.nacse.org/research/airlichen/workgroup/>
- Gertler, A.W., Bytnerowicz, A., Cahill, T.A., Arbaugh, M., Cliff, S., Kahyaoglu-Koračin, J., Tarnay, L., Alonso, R., and Fraczek, W. 2006. Local air pollutants threaten Lake Tahoe's clarity. *Calif. Agric.* 60, 53–58.
- Glaubig, R., and Gomez, A. 1994. A simple, inexpensive rain and canopy throughfall collector. *J. Environ. Qual.* 23, 1103–1107.
- Grell, G.A., Dudhia, J., and Stauffer, D.R. 1994. A description of the fifth-generation Penn State/NCAR Mesoscale Model (MM5). National Center for Atmospheric Research Technical Note NCAR/TN-398_STR, 138 pp. Available from NCAR, P.O. Box 3000, Boulder, CO, 80307, USA.
- Hansen, S., and Davies, M.A. 2002. Windshields for precipitation gauges and improved measurement techniques for snowfall. Tech Tip 0225-2325-MTDC. Missoula, MT: U.S. Department of Agriculture, Forest Service, Missoula Technology and Development Center, Missoula, MT, USA.
- Harrington, R., and Bales, R.C. 1998. Modeling ionic solute transport in melting snow. *Water Resour. Res.* 34, 1727–1736.
- Holland, E.A., Braswell, B.H., Sulzman, J., and Lamarque, J.F. 2005. Nitrogen deposition onto the United States and western Europe: Synthesis of observations and models. *Ecol. Appl.* 15, 38–57.
- Houle, D., Ouimet, R., Paquin, R., and Laflamme, J.G. 1999. Determination of sample size for estimating ion throughfall deposition under a mixed hardwood forest at the Lake Clair Watershed (Duchesnay, Quebec). *Can. J. Res.* 29, 1935–1943.
- Hunsaker, C.T., and Eagan, S.M. 2003. Small stream ecosystem variability in the Sierra Nevada of California. In: Renard, K.G., McElroy, S.A., Gburek, W.J., Canfield, H.E., Scott, R.L., eds. First interagency conference on research in the watersheds, 27–30 October 2003. U.S. Department of Agriculture, Agricultural Research Service, pp. 716–721. <http://www.tucson.ars.ag.gov/icrw/Proceedings/Hunsaker.pdf>
- Ingersoll, G.P., Turk, J.T., Mast, M.A., Clow, D.W., Campbell, D.H., and Bailey, Z.C. 2002. Rocky Mountain snowpack chemistry network: history, methods, and the importance of monitoring mountain ecosystems. U.S. Geological Survey Open-File 01-466. Geological Survey Acid Rain Quality-Assurance Project. U.S. Geological Survey Water-Resources Investigations Report 90-4029.
- Johnson, D.W., and Lindberg, S.E., eds. 1992. Atmospheric deposition and forest nutrient cycling. *Ecological studies* 91. Springer, New York.
- Jun, M., and Stein, M.L. 2004. Statistical comparison of observed and CMAQ modeled daily sulfate levels. *Atmos. Environ.* 38, 4427–4436.
- Kendall, C., and McDonnell, J.J., eds. 1998. Isotope tracers in catchment hydrology. Elsevier Science, Amsterdam, The Netherlands.
- Kester, C.L., Baron, J.S., and Turk, J.T. 2003. Isotopic study of sulfate sources and residence times in a subalpine watershed. *Environ. Geol.* 43, 606–613.
- Kolian, M., and Haeuber, R. 2004. Clean air status and trends network (CASTNet)—Air-quality assessment and accountability. In: Wiersma, G.B., ed. *Environmental monitoring*. CRC Press, Boca Raton, FL, pp. 685–718.

- König, M., Winther, J.G., and Isaksson, E. 2001. Measuring snow and glacier ice properties from satellite. *Rev. Geophys.* 3, 1–27.
- Koutrakis, P., Wolfson, J.M., Bunyaviroch, A., Froelich, S.E., Hirano, K., and Mulik, J.D. 1993. Measurement of ambient ozone using a nitrite-coated filter. *Anal. Chem.* 65, 209–214.
- Krupa, S.V. 2002. Sampling and physico-chemical analysis of precipitation: A review. *Environ. Pollut.* 120, 565–594.
- Krupa, S.V., and Legge, A.H. 2000. Passive sampling of ambient, gaseous air pollutants: An assessment from an ecological perspective. *Environ. Pollut.* 107, 31–45.
- Landers, D.H., Simonich, S.L., Campbell, D.H., Erway, M.M., Geiser, L.H., Jaffe, D.A., Kent, M.L., Schreck, C.B., Blett, T.F., and Taylor, H.E. 2003. Western airborne contaminants assessment project research plan: U.S. environmental protection agency, Office of Research and Development, NHEERL, Western Ecology Division, EPA/600/R-03/035.
- Lawrence, G.B., and Fernandez, I.J. 1993. A reassessment of areal variability of throughfall deposition measurements. *Ecol. Appl.* 3, 473–480.
- Leydecker, A., and Melack, J.M. 1999. Evaporation from snow in the central Sierra Nevada of California. *Nordic Hydrol.* 30, 81–108.
- Ling, C.H., Josberger, E.G., and Thorndike, A.S. 1996. Mesoscale variability of the upper Colorado River snowpack. *Nordic Hydrol.* 27, 313–322.
- Lovett, G.M. 1994. Atmospheric deposition of nutrients and pollutants in North America: An ecological perspective. *Ecol. Appl.* 4, 629–650.
- Lovett, G.M., and Lindberg, S.E. 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. *Can. J. Res.* 23, 1603–1616.
- Marques, M.C., Gravenhorst, G., and Ibrom, A. 2001. Input of atmospheric particles into forest stands by dry deposition. *Water Air Soil Pollut.* 130, 571–576.
- Mast, M.A., Turk, J.T., Ingersoll, G.P., Clow, D.W., and Kester, C.L. 2001. Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks. *Atmos. Environ.* 35, 3303–3313.
- Mcardle, N.C., and Liss, P.S. 1995. Isotopes and atmospheric sulfur. *Atmos. Environ.* 29, 2553–2556.
- Mebust, M.R., Eder, B.K., Binkowski, R.S., and Roselle, S.J. 2003. Models-3 community multiscale air quality (CMAQ) model aerosol component, 2. Model evaluation. *J. Geophys. Res.* 108, 4184, doi:10.1029/2001KD001410.
- Melack, J.M., and Sickman, J.O. 1997. Monitoring of wet deposition in alpine areas in the Sierra Nevada, Final report, contract, A932-081, California Environmental Protection Agency, Air Resources Board, Research Division, Sacramento, CA, USA.
- Michalski, G., Meixner, T., Fenn, M., Hernandez, L., Sirulnik, A., Allen, E., and Thiemens, M. 2004. Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using $\Delta^{17}\text{O}$. *Environ. Sci. Technol.* 38, 2175–2181.
- Michel, R.L., Turk, J.T., Campbell, D.H., and Mast, M.A. 2002. Use of natural ^{35}S to trace sulphate cycling in a small lake in the Flattops Wilderness Area, Colorado, USA. *Water Air Soil Pollut.: Focus* 2, 5–18.
- Molotch, N.P., and Bales, R. 2005. Scaling snow observations from the point to the grid element: Implications for observation network design. *Water Resour. Res.* 41, W11421, doi:10.1029/2005WR004229.
- Molotch, N.P., Fassnacht, S.R., Bales, R.C., and Helfrich, S.R. 2004a. Estimating the distribution of snow water equivalent and snow extent beneath cloud-cover in the Salt-Verde River basin, Arizona. *Hydrologic. Proc.* 18, 1595–1611.
- Molotch, N.P., Painter, T.H., Bales, R.C., and Dozier, J. 2004b. Incorporating remotely sensed snow albedo into a spatially distributed snowmelt model. *Geophys. Res. Lett.* 31, doi:10.1029/2003GL019063.

- Molotch, N.P., Colee, M.T., Bales, R.C., and Dozier, J. 2005. Estimating the spatial distribution of snow water equivalent in an alpine basin using binary regression tree models: The impact of digital elevation data and independent variable selection. *Hydrologic. Proc.* 19, 1459–1479.
- Mosello, R., Marchetto, A., and Tartari, G.A. 1988. Bulk and wet atmospheric deposition chemistry at Pallanza N. Italy. *Water Air Soil Pollut.* 42, 137–151.
- Naftz, D.L., Schuster, P.F., and Reddy, M.M. 1994. Assessment of spatial variability of major-ion concentrations and DEL oxygen-18 values in surface snow, upper Fremont Glacier, WY, USA. *Nordic Hydrol.* 25, 371–388.
- Naftz, D.L., Susong, D.D., Schuster, P.F., Cecil, D., Dettinger, M.D., Michel, R.L., and Kendall, C. 2002. Ice core evidence of rapid air temperature increases since 1960 in alpine areas of the Wind River Range, Wyoming, United States. *J. Geophys. Res.* 107(D13), 4171, doi:10.1029/2001JD000621.
- Nanus, L., Campbell, D.H., Ingersoll, G.P., Clow, D.W., and Mast, M.A. 2003. Atmospheric deposition maps for the Rocky Mountains. *Atmos. Environ.* 37, 4881–4892.
- Ogawa & Co., USA, Inc. 1998. NO, NO₂, NO_x and SO₂ sampling protocol using the ogawa sampler. Users' Guide, version 4.0, February, 1998. Ogawa & Company, Pompano Beach, FL.
- Padgett, P.E. 2004. Vegetation as passive collectors ... maybe not. In: Douglas, K.E., and Bedient, P.S., eds. *Proceedings of National Atmospheric Deposition Program Technical Committee Meeting and Scientific Symposium*. 21–23 September 2004, Halifax, Nova Scotia, Canada, 46 pp. <http://nadp.sws.uiuc.edu/lib/proceedings/NADPpro2004.pdf>
- Padgett, P.E., and Bytnerowicz, A. 2001. Deposition and adsorption of the air pollutant HNO₃ vapor to soil surfaces. *Atmos. Environ.* 35, 2405–2415.
- Padgett, P.E., Allen, E.B., Bytnerowicz, A., and Minich, R.A. 1999. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. *Atmos. Environ.* 33, 769–781.
- Padgett, P.E., Bytnerowicz, A., Dawson, P.J., Riechers, G.H., and Fitz, D.R. 2004. Design, evaluation and application of a continuously stirred tank reactor system for use in nitric acid air pollutant studies. *Water Air Soil Pollut.* 151, 35–51.
- Pathak, R.K., and Chan, C.K. 2005. Inter-particle and gas-particle interactions in sampling artifacts of PM_{2.5} in filter-based samplers. *Atmos. Environ.* 39, 1597–1607.
- Pleim, J.E., Xiu, A., Finkelstein, P.L., and Otte, T.L. 2001. A coupled land-surface and dry deposition model and comparison to field measurements of surface heat, moisture, and ozone fluxes. *Water Air Soil Pollut.: Focus* 1, 243–252.
- Ranalli, A.J., Turk, J.T., and Campbell, D.H. 1997. The use of bulk collectors in monitoring wet deposition at high-altitude sites in winter. *Water Air Soil Pollut.* 95, 237–255.
- Ray, J.D. 2001. Spatial distribution of tropospheric ozone in national parks of California: Interpretation of passive-sampler data. *ScientificWorld* 1, 483–497.
- Roadman, M.J., Scudlark, J.R., Meisinger, J.J., and Ullman, W.J. 2003. Validation of Ogawa passive samplers for the determinations of gaseous ammonia concentrations in agricultural settings. *Atmos. Environ.* 37, 2317–2325.
- Savard, M. 2005. Sulfate and nitrate deposition to balsam fir measured across an elevational gradient on Mt. Washington, White Mountains, New Hampshire. Undergraduate Thesis. Princeton University, Department of Ecology and Evolutionary Biology, Princeton, NJ, USA.
- Schmitt, M., Thoni, L., Waldner, P., and Thimonier, A. 2005. Total deposition of nitrogen on Swiss long-term forest ecosystem research (LWF) plots: Comparison of the throughfall and the inferential method. *Atmos. Environ.* 39, 1079–1091.

- Scire, J.S., Strimaitis, D.G., and Yamartino, R.J. 2000. A user's guide for the CALPUFF dispersion model (Version 5.4). Earth Tech, Inc., Concord, MA.
- Seinfeld, J.H., and Pandis, S.N. 1998. Atmospheric chemistry and physics. Wiley, New York.
- Shanley, J.B. 1989. Field measurements of dry deposition to spruce foliage and Petri dishes in the Black Forest, F.R.G. *Atmos. Environ.* 23, 403–414.
- Sickman, J.O., Leydecker, A., and Melack, J.M. 2001. Nitrogen mass balances and abiotic controls on N retention and yield in high-elevation ecosystems of the Sierra Nevada, California, USA. *Water Resour. Res.* 37, 1445–1461.
- Simkin, S.M., Lewis, D.N., Weathers, K.C., Lovett, G.M., and Schwarz, K. 2004. Determination of sulfate, nitrate, and chloride in throughfall using ion-exchange resins. *Water Air Soil Pollut.* 153, 343–354.
- Simpson, D., Fagerli, H., Hellsten, S., Knulst, J.C., and Westling, O. 2006. Comparison of modelled and monitored deposition fluxes of sulphur and nitrogen to ICP-forest sites in Europe. *Biogeosciences* 3, 337–355.
- Swall, J.L., and Davis, J.M. 2006. A Bayesian statistical approach for the evaluation of CMAQ. *Atmos. Environ.* 40, 4883–4893.
- Tang, H. 2001. Introduction of Maxxam all-season passive sampling system and principles of proper use of passive samplers in the field study In: *Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research*, 9 April 2001, Riverside, California, USA. *ScientificWorld* 1, 463–474.
- Thimonier, A. 1998. Measurement of atmospheric deposition under forest canopies: Some recommendations for equipment and sampling design. *Environ. Monit. Assess.* 52, 353–387.
- Tonnesen, G., and Wang, Z. 2005. Assessment of nitrogen deposition: Modeling and habitat assessment, Draft Report, California Energy Commission, Sacramento, CA, USA.
- Tonnesen, G., Wang, Z., Omary, M., and Chien, C.J. 2003. Formulation and application of regional air quality modeling for integrated assessments of urban and wildland pollution. In: Bytnerowicz, A., Arbaugh, M.J., and Alonso, R., eds. *Developments in environmental science, volume 2: Ozone air pollution in the Sierra Nevada: Distribution and effects on forests*. Elsevier, Amsterdam, The Netherlands, pp. 299–324.
- Turk, J.T., Taylor, H.E., Ingersoll, G.P., Tonnessen, K.A., Clow, D.W., Mast, M.A., Campbell, D.H., and Melack, J.M. 2001. Major-ion chemistry of the Rocky Mountain snowpack, USA. *Atmos. Environ.* 35, 3957–3966.
- Wadleigh, M.A., Schwarcz, H.P., and Kramer, J.R. 1996. Isotopic evidence for the origin of sulphate in coastal rain. *Tellus Series B* 48, 44–59.
- Waldman, J.M., Munger, J.W., Jacob, D.J., and Hoffmann, M.R. 1985. Chemical characterization of stratus cloudwater and its role as a vector for pollutant deposition in a Los Angeles pine forest. *Tellus* 37B, 91–108.
- Weathers, K.C. 1999. The importance of cloud and fog to the maintenance of ecosystems. *Trends Ecol. Evol.* 14, 214–215.
- Weathers, K.C., and Likens, G.E. 1997. Clouds in southern Chile: An important source of nitrogen to nitrogen-limited ecosystems? *Environ. Sci. Technol.* 31, 210–213.
- Weathers, K.C., Likens, G.E., Bormann, F.H., Bicknell, S.H., Bormann, B.T., Daube, B.C., Eaton, J.S., Galloway, J.N., Keene, W.C., Kimball, K.D., McDowell, W.H., Siccamo, T.G., Smiley, D., and Tarrant, R.A. 1988. Cloudwater chemistry from 10 sites in North America. *Environ. Sci. Technol.* 22, 1018–1026.
- Weathers, K.C., Lovett, G.M., and Likens, G.E. 1992. The influence of a forest edge on cloud deposition. In: Schwartz, S.E., and Slinn, W.G.N., eds. *Precipitation scavenging and atmosphere-surface exchange. Vol. 3—The summers volume: Applications and appraisals*. Hemisphere Publishing Corporation, Bristol, PA, pp. 1415–1423.

- Weathers, K.C., Lovett, G.M., and Likens, G.E. 1995. Cloud deposition to a spruce forest edge. *Atmos. Environ.* 29, 665–672.
- Weathers, K.C., Lovett, G.M., Likens, G.E., and Lathrop, R. 2000. The effect of landscape features on deposition to Hunter Mountain, Catskill Mountains, New York. *Ecol. Appl.* 10, 528–540.
- Weathers, K.C., Cadenasso, M.L., and Pickett, S.T.A. 2001. Forest edges as nutrient and pollutant concentrators: Potential synergisms between fragmentation, forest canopies, and the atmosphere. *Conserv. Biol.* 15, 1506–1514.
- Weathers, K.C., Simkin, S.M., Lovett, G.M., and Lindberg, S.E. 2006. Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecol. Appl.* 16, 1590–1607.
- Wesely, M.L., and Hicks, B.B. 2000. A review of the current status of knowledge on dry deposition. *Atmos. Environ.* 34, 2261–2282.
- Williams, M.W., Bardsley, T., and Rikkers, M. 1998. Overestimation of snow depth and inorganic nitrogen wetfall using NADP data, Niwot Ridge, Colorado. *Atmos. Environ.* 32, 3827–3833.
- Winstral, A., Elder, K., and Davis, R.E. 2002. Spatial snow modeling of wind-redistributed snow using terrain-based parameters. *J. Hydrometeorol.* 3, 524–538.